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**Chemistry.** — "*An electrical, adiabatic calorimeter and its use in the determination of heats of solution.*" By Prof. ERNST COHEN, Dr. A. L. TH. MOESVELD and Dr. W. D. HEIDERMAN.

(Communicated at the meeting of May 31, 1924).

### *Introduction.*

1. A few years ago ERNST COHEN and A. L. TH. MOESVELD described an adiabatic, electrical calorimeter<sup>1)</sup> for the determination (with an accuracy of 0.05 %) of the true specific heat of solutions, and somewhat later, in another paper, it was shown that the true specific heat of solids can also be accurately measured with this apparatus<sup>2)</sup>.

As the accuracy of the determinations of the heats of solution of a great number of substances is anything but satisfactory, we have adapted the calorimeter, above mentioned, for similar determinations, and in this paper shall give a description of the apparatus, and, in order to illustrate its use, the process of determining a heat of solution will be described.

As the apparatus resembles in many respects the instrument described in the paper mentioned we shall put special stress on the particulars in which it differs from the apparatus then described.

We wish to observe that the principle which was applied in this case has already been made use of by ERNST COHEN and A. L. TH. MOESVELD in the determination of the heat of solution of m. dinitrobenzene in aethyl-acetate when experimentally testing the law of BRAUN<sup>3)</sup>. In that paper they also drew attention to the investigations of BRÖNSTED and those of VON STEINWEHR. The apparatus to be described below may be considered as an improved form of our adiabatic, electrical calorimeter.

To elucidate the principle in question we shall give a short exposition of it. If the negative heat of solution of a substance *A* in a solvent *B* is to be determined we put the solvent and the substance to be dissolved in one or more glass bulbs, in a completely closed calorimeter which stands in a surrounding of constant temperature. When thermal equilibrium has been established between the calorimeter with its contents and the surroundings, the bulbs are crushed from the outside. Care is taken to maintain the temperature of the calori-

<sup>1)</sup> These Proc. **28**, 883 (1920). Zeitschr. f. physik. Chemie **95**, 305 (1920).

<sup>2)</sup> Zeitschr. f. physik. Chemie **100**, 151 (1922).

<sup>3)</sup> These Proc. **26**, 1553 (1918); Zeitschr. f. physik. Chemie **93**, 385 (1919); especially § 93.

meter by supplying it with the necessary quantity of electric energy. Contingent small variations during the process of solution are read from a thermometer placed in the calorimeter, and taken into consideration. In this way the negative heat of solution is compensated by the electric energy (corrected for the small changes of temperature mentioned above) and the heat of solution is found by measuring the electric energy. If the heat of solution to be determined is positive, the same apparatus may be used, but in a totally different way. In a future paper we shall treat this subject further, and in the present discuss only the determination of negative heats of solution.

Fig. 1 is a diagrammatic sketch of the complete apparatus.

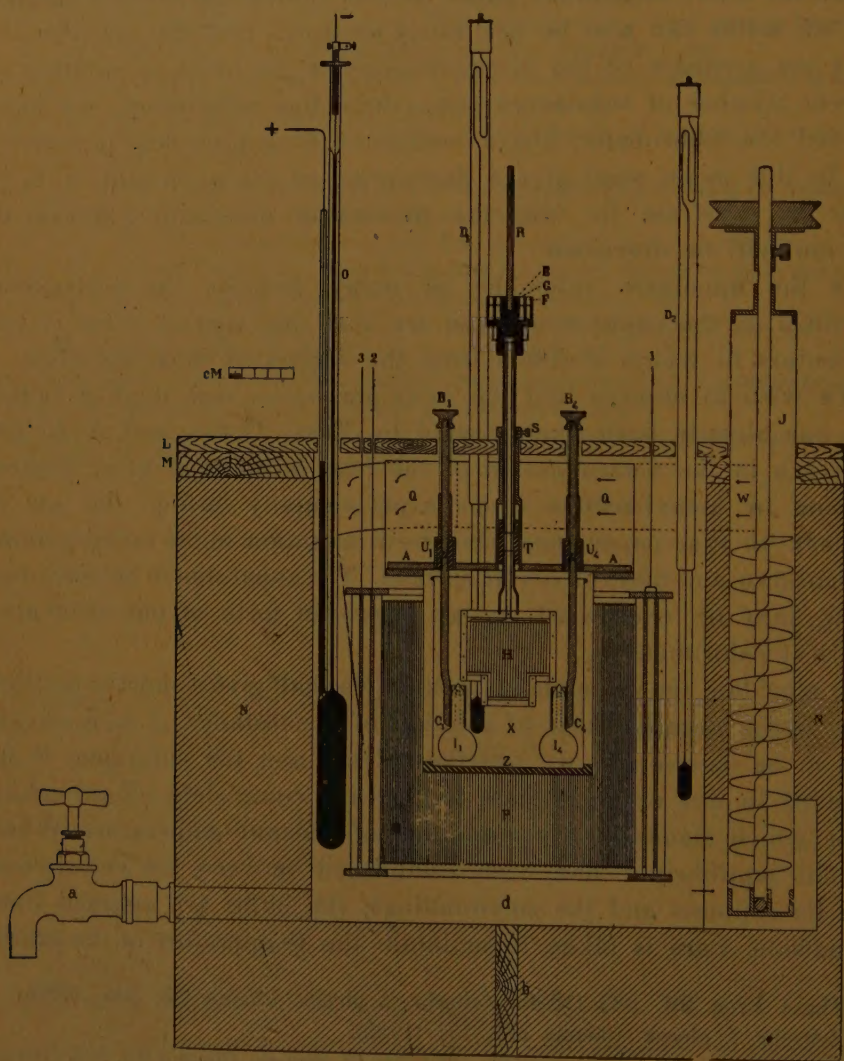


Fig. 1.



### The Calorimeter.

2. The calorimeter itself (X, Fig. 1) is a cylindrical vessel of copper, washgilded, (contents  $\pm 1350$  cc.). As in the course of time most salt solutions affect the underlying copper, the layer of gold is covered with a layer of varnish; for this purpose we used "*Valspar enamel*", a preparation which gave very satisfactory results.

3. The calorimeter rests in the hollow of an ebonite disc, the latter fits accurately in the cylinder of copper, which serves as air jacket. This cylinder passes into a wider cylinder; the flat ring which connects the two cylinders supports the brass lid *AA*. When the lid is in position during the experiment the space over it is filled up with cotton-wool, which forms a thorough insulation of the lid.

4. In fig. 2 this lid is shown separately with the stirrer and the construction which enabled us to crush one by one the bulbs containing the salt to be dissolved, after thermal equilibrium was established in the calorimeter.

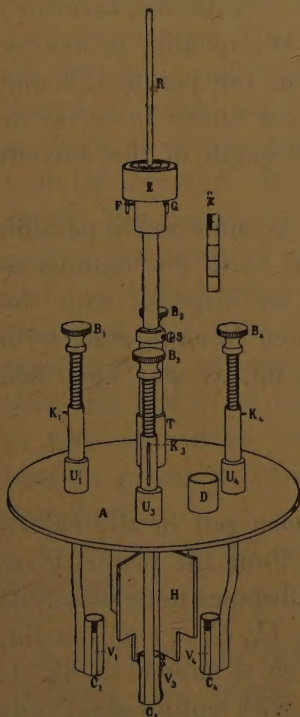


Fig. 2.

Through the four tubes  $U_1, U_2, U_3, U_4$ , three of which are visible in the sketch, pass the copper rods  $K_1, K_2, K_3$ , and  $K_4$ . At the place where these rods enter the tubes a piece of ebonite is placed between their upper and lower parts to prevent conduction of heat as much as possible. These rods cannot turn in the tubes in which they move, because a copper pin, adjusted vertically on the axis, moves up and down in a groove in the tube. The bulbs whose stems are stuck in the tubes  $C_1, C_2, C_3$ , and  $C_4$ , are prevented from turning by this adjustment, as they might easily be broken against the walls of the calorimeter if any turning should occur. The necks of the bulbs are kept in place in the tubes  $C_1, \dots$  by springs  $V_1, V_2, V_3$ , and  $V_4$ . The spiral springs  $K_1, K_2, \dots$  hold up the tubes  $C_1, C_2, \dots$ . The stirrer  $R$  passes through the shaft  $T$ .

The wings of the stirrer  $H$ , which also functions as heater, are shaped in such a way that the stirrer can turn freely between the bulbs. The description of the construction of the stirrer may be found in the paper, mentioned above, on the determination of the

specific heat of solid substances especially in § 5<sup>1</sup>). When the bulbs are to be crushed a blow with a small hammer is given on the heads  $B_1, B_2$ , etc. The spiral springs cause the rods to rise again after the bulbs have been crushed.

5. The paraffin oil which surrounds the air jacket is stirred with the stirrer  $I$  (screw of Archimedes) which is kept in motion by an electric motor ( $\pm 1900$  revolutions per minute)<sup>2</sup>). The paraffin oil flows from the vessel  $d$  through an opening in the wall of this vessel (between the two arrows) to the stirrer, is sucked upwards, and at  $W$  enters the channel  $QQ$ , through which it flows back to  $d$ . The temperature is regulated with the electric regulator  $O$  (already described by us). [By means of relays the current of the municipal power station (220 Volt D.C.) which heats the heating-net  $P$ , after passing through several electric lamps, is connected up or switched off]. This heater, made of nickel wire, woven in asbestos, furnished by the firm SCHNIEWINDT at Neuenrade in Westphalia, in reality consists of two separate nets. By connecting up the points 1, 2, and 3 in different ways, one net, or two circuits either in series or parallel, may be connected up, and so the strength of the current may be varied at will.

During the whole experiment the air jacket is immersed in paraffin oil which is kept at a constant temperature (with fluctuations of about  $0^{\circ}.01$ ). By using the electric regulator we dispense with the part  $\dagger, U_1 W_2, S_1, S_2$ ,—, drawn in fig. 3, which is connected with the supply of electric energy to the paraffin oil, as was described in a former paper.

### *Method of Manipulation.*

6. When the solvent (after weighing) has been put in the calorimeter, we place this vessel in the air jacket. Four (or fewer) glass bulbs with very thin bottoms, in which the substance to be dissolved is weighed, are sealed and put in the tubes  $C_1, C_2$ , ... of the lid, and this cover is placed on the copper rim, as is shown in fig. 1. Then the space above the cover is filled up with cotton-wool, and the apparatus is closed with the wooden cover  $L$ .

When the stirrers  $R$  and  $I$  have been set in motion, the paraffin oil is heated by connecting the heating net with the current from the power-station, and kept at such a definite temperature  $A$  that

<sup>1</sup>) Zeitschr. f. physik. Chemie 100, 151 (1922).

<sup>2</sup>) ERNST COHEN and A. L. TH. MOESVELD, Zeitschr. f. physik. Chemie 93, 385 (1919), especially § 47 seq.



the contents of the calorimeter may have exactly the constant temperature  $B$  at which the experiment is to be carried out. If necessary a small current is sent through the heating stirrer  $H$  in order to accelerate thermal equilibrium between the calorimeter and its surroundings. If this equilibrium is obtained, (i.e. if the reading of the BECKMANN<sup>1)</sup> thermometer with  $0^{\circ}.01$  intervals  $D_1$  remains constant for  $\frac{1}{2}$  hour within  $0^{\circ}.001$ — $0^{\circ}.002$ ) the experiment proper can begin.

7. By reversing the switch  $P_1$  (fig. 3) we allow current to pass through the stirrer into the calorimeter, until the temperature of the latter rises through about one half of the number of degrees of temperature change which would be observed during the solution of the salt of the first bulb, if no electric energy were sent into the calorimeter. This number is determined by a preliminary test<sup>2)</sup>. Then the first bulb is crushed by giving a blow on the head  $B_1$ . For the moment the temperature falls in consequence of the dissolving of the salt, and then rises again, as electric energy is continually passed through the heating stirrer. When the temperature is again as high as it was before the crushing of the first bulb, the second bulb is crushed, etc. When the contents of the last bulb are dissolved the resistance in the resistance-box  $W_1$  is raised (fig. 3), (noting the time) so as to reach thermal equilibrium more slowly, and just before reaching this point the current is switched off again recording the time. When thermal equilibrium has been finally reached it is necessary to control the constancy of the thermometer, then the E.M.F. of the accumulator in the potentiometer is measured, as was also done before the experiment, and the resistance of the heating stirrer is controlled in the way that has been previously described<sup>3)</sup>.

For the method of computation we refer to the paper already mentioned.

8. In order to illustrate the procedure we shall describe an experiment, the object of which was to determine at  $32^{\circ}.3$  C. (in connection with an investigation to be described later on) the heat of solution of  $\text{NH}_4\text{NO}_3$  in a solution of ammonium nitrate which already contained 40.30 gr. of salt per 100 gr. of solution, the concentration then rising to 42.30 in the same units.

<sup>1)</sup> This thermometer had been controlled by the Phys. Techn. Reichsanstalt at Charlottenburg-Berlin.

<sup>2)</sup> Zeitschr. f. physik. Chemie 93, 385 (1919), especially § 114 et seq.





TABLE I.

Time	Readings of the thermometer in the calorimeter	Readings potentiometer
2.45	4.080	—
50	4.080	—
55	4.080	—
3.00	4.080	—
At 3.00 the current is connected up in the stirrer.		136.73
3.01	4.180	136.74
02	4.320 1st bulb crushed	136.74
03	3.950	136.74
04	4.100	136.73
05	4.240 2nd bulb crushed	136.73
06	3.915	136.73
07	4.035	136.74
08	4.170 3rd bulb crushed	136.72
09	3.820	136.72
10	3.970	136.72
11	4.110	136.72
12	4.250 4th bulb crushed	136.72
13	3.905	136.72
14	4.050 resistance connected up	56.84
At 3.14min.18.8sec. current switched off in stirrer.		
3.15	4.090	—
16	4.090	—
17	4.090	—
18	4.090	—
19	4.090	—

At the commencement of the experiment the reading in the potentiometer for the CLARK-element was 126.75, and the final reading was 126.74. For the two WESTON-elements 90.88 and 90.88, respectively 90.87 and 90.87. The value of 1.0181 Volt is taken as the E. M. F. of the Weston-element at that temperature. The value of 0.2389 gr. cal. is taken for one Joule. The resistance of the heating stirrer was 23.993  $\Omega$ , the radiation constant of the calorimeter 0.0065 degree-minute and the water equivalent of the calorimeter (determined electrically) 121.3.

From the table it can be seen, that the electric energy has been sent into the calorimeter in two stages. During 840 seconds with an E. M. F. of <sup>1)</sup>

$$\frac{136.73}{90.88} \times 9.9975 \times 1.0181 = 15.313 \text{ Volt,}$$

and during 18.8 seconds with an E. M. F. of

$$\frac{56.84}{90.88} \times 9.9975 \times 1.0181 = 6.366 \text{ Volt.}$$

<sup>1)</sup> Comp. Zeitschr. f. physik. Chemie 93, 385 (1919), especially § 114 et seq.

Total quantity of electric energy:

$$\left( \frac{15.313^2}{23.993} \times 840 + \frac{6.366^2}{23.993} \times 18.8 \right) 0.2389 \text{ gr. calories} = 1969.1 \text{ gr. cal.}$$

Further we find for the radiation correction

$$(4.085 + 57.015 - 15 \times 4.080) 0^{\circ}.0065 = -0^{\circ}.00065.$$

The final temperature was  $0^{\circ}.010$  too high, so that the total temperature correction will be  $0^{\circ}.010$ <sup>1)</sup>. We must subtract the corresponding quantity of heat from the heat sent electrically into the calorimeter.

As the water equivalent of the solution (specific heat<sup>2)</sup> 0.7246) is  $1240.9 \times 0.7246$ , the water equivalent of the calorimeter 121.3, of the glass of the bulbs 3.5, the total water equivalent is 1023.9, and the necessary correction  $-1023.9 \times 0.01 = -10.2$  gr. cal. The total quantity of energy which was supplied is now  $1969.1 - 10.2 = 1958.9$  gr. cal. So we find for the heat of solution per gram-molecule  $\text{NH}_4\text{NO}_3$  (80.1 gr.) in the solution in question:

$$-\frac{80.1}{43.8249} \times 1958.9 = -3581 \text{ gr. calories.}$$

The result of a second experiment was: — 3587.

A third determination gave: — 3589 gr. cal.

The agreement is thus very satisfactory.

9. Finally a few observations on the accuracy of the method described. If the accuracy of the reading of the thermometer is assumed to be  $0^{\circ}.001$  and the substance dissolved would have produced, if uncompensated a temperature change of one degree, the accuracy would be about 0.2 %. If the viscosity of the solution becomes considerably greater after dissolving the salt, so that the friction of the stirrer in the liquid increases, this should also be taken into account. The error in the measurement of the E. M. F. which play a part in the experiment, as well as the error of the resistance of the heating-wire may amount to some hundredths of one percent, the error in the measurement of the time, during which the current passes through the stirrer, may give rise to discrepancies in the heat of solution, which are of the same order of magnitude as those of the reading of the thermometer.

In a series of experiments, similar to the one described in this paper, and to which we shall return later on in another connection, the accuracy proved to be 0.3 %.

## S U M M A R Y.

The adiabatic, electrical calorimeter, described by us in a previous paper, has been modified for the purpose of measuring heats of solution, and an accuracy of about 0.3 %, has been obtained.

*Utrecht, May 1924.*

*VAN 'T HOFF-Laboratory.*

1) In this case the very small amount of  $0^{\circ}.00065$  degrees is neglected.

2) Comp. these Proceedings 33, 358 (1924).



**Botany.** — "*Methodic Precautions in Further Analysis of Light-growth-response.*" By M. PINKHOF. (Communicated by Prof. A. H. BLAAUW).

(Communicated at the meeting of September 27, 1924.)

Changes in the intensity of light, falling on such part of a plant as is sensible for it, will primarily produce there internal changes. These, on their turn, will secondarily induce externally visible alterations in the course of growth, the so-called "light-growth-response", which is the first subject of research in this instance, being a less difficult object of examination as compared with the primary internal changes.

BLAAUW has proclaimed a relation between the light-growth-response and the phototropical curvations. His researches were followed by those of many others, who, by different methods, tried to ascertain the validity of BLAAUW's theory. They nearly all used the same object, viz. the coleoptile of the *Avena* seedlings, which circumstance enables to comparison of results.

The plan of researches of this kind is formulated by BRAUNER (3, page 497) as follows: "(Man wird) zur Ergründung des Problems der Lichtkrümmung von der Untersuchung auszugehen haben, ob allseitige Lichtwirkung die Pflanze zu einer Wachstumsänderung veranlasst, die der beobachteten Krümmung entspricht."

BRAUNER has nearly succeeded in designing a correspondence between the phenomena meant here: light-growth-response and phototropical curvature. Even had the result been a negative, BRAUNER would have been entitled to draw conclusions from it, comparing as he did one-sided with all-sided effects of the same external influence (light) on the same organic object (*Avena*-coleoptile as a whole) and in both cases he judged the effect at the course of the externally visible resultants of the internal changes.

At a recently published research, BRAUNER (4) makes further progress and tries (1) to give a measurable shape to one of the *internal* changes (viz. the permeability of protoplasm); and (2) to investigate, whether or not it goes parallelly with the light-curvature-reaction and the light-growth-response. From this he wishes to draw a conclusion as to its eventual share in these reactions. Here, in my opinion, BRAUNER makes a methodical error. He compares the changes in one of the components with those in the resultant. So as to make this clear, I have first to give a brief survey of his method.

During three hours he examines at every fifteen minutes in an *Avena*-coleoptile the resistance, met with by a feeble electric current at passing a part of 1 mm. in length, situated at 2 mm. distance from the top. He supposes this resistance to be a measure for the permeability of the protoplasm. He then compares the course, shown by this resistance in respect of plants in the dark and of plants illuminated in a certain way. The difference (decrease of resistance under influence of light) he illustrates graphically and he compares the curve with the graphs of light-growth-response and light-curvature. He, then, finds no resemblance with the first, and some with the second.

The little known to us about the complex of internal changes induced in the *Avena*-coleoptile by illumination, is sufficient to make us realise its complicity. BRAUNER considers the millimeter examined by him as the most sensible part of the coleoptile. He submits it to light and after 15 minutes he states a change in permeability. Meanwhile, a stimulation has left the top for lower situated parts of the coleoptile and there gives rise to changes, which, if not qualitatively, will differ quantitatively and which, moreover, occur at different moments. These changes are judged every 15 minutes by their collective resultant: the change in the total length of the coleoptile (respectively the change of the angle between the upper part and the vertical line). Now, in my opinion, it is not allowed to compare the course of this resultant with that, shown by the permeability of a small part of the coleoptile. One could imagine, in case of a light-push, that up there the permeability will soon be normal again, whilst the results of her temporary deviation will be perceptible even a long time afterwards in the light-growth-response as executed by the whole coleoptile. Or, in case of uninterrupted illumination, that the permeability there will have undergone, after some time, a maximum increase (as it cannot go on increasing continuously); whilst again the results of the changes will be expressed by the whole coleoptile in a complicated way.

*Simultaneous and equally directed changes in the quantities compared by BRAUNER, are, consequently, not to be expected, but their staying out neither tells us anything.*

Meanwhile, BRAUNER's researches would retain this result, that illumination increases the permeability of protoplasm.

This has been shown already for other parts of plants (tree leaves) by TRÖNDLE (8), and probably applies to the *Avena*-coleoptile as well. Nevertheless the method used by BRAUNER does not seem to give fully useful results in my opinion. It has been applied following



the researches described by SMALL (6) about changes in permeability under geotropic stimulation. In the supposition of the constancy of the number of ions between the electrodes it may be assumed, that changes in resistance are dependent on changes in permeability of the protoplasm and consequently are a measure of the latter. According to SMALL's method for roots of *Vicia Faba*, BRAUNER pierces the coleoptile from both sides by the platinum wires of 0.1 mm. thickness. He, then, covers it wholly by a thin layer of paraffine (melting-point  $38^{\circ}$  Cels.) and further examines the resistance every 15 minutes. With seedlings in the dark he, now, does not find a constant resistance, but a gradually increasing one. This he calls the normal case and attributes the increase to the influence of the measuring current (SMALL thinks the interval of 15 minutes sufficient to eliminate such an influence for his object). Now, at his light experiments, BRAUNER states not a decrease of resistance, but a *less important increase*.

The fact, that in practically all cases the resistance appeared to increase, suggested to me the question, whether perhaps a condition has remained unfulfilled, which, evident as it may seem, still ought not to be overlooked: viz. the constant distance of the electrodes. For, if the coleoptile continues its growth in the area of the electrodes as well, the latter may come at larger distance within the duration of the experiment; so that an increase of resistance would be explained. The observations of ROTHERT (5, p. 28) took place with too large intervals to be used as a measure here. I therefore have tried to obtain data by means of a simple experiment. I cultivated *Avena* seedlings in the constant room of the Laboratory under the same circumstances as BRAUNER did (3, p. 499). However, I was not able to make use of seeds of a "pure line". So as to make quantitative comparisons, one should, in fact, always work with the same "pure line". In the same way as BRAUNER I furnished the coleoptiles with a small cap of paraffine, melting-point  $38^{\circ}$  Cels. The temperature was  $19^{\circ}.5$  to  $20^{\circ}$  Cels.

In the following way I obtained a scale on the paraffine cap. I for one moment pressed against it a sharp edged screw (thread distance exactly 1 mm.). The advantage of this is, that at the beginning of the measuring no reading needs to be done. A hard rubber screw may eventually also be used for printing ink marks at equal distances on the coleoptiles themselves.

After the seedlings had remained in the dark for still 3 hours, I measured with a horizontal microscope the distance between the 2<sup>nd</sup> and the 3<sup>rd</sup> mark.

In a series of 6 ex. (17<sup>th</sup> June) the increase was 20.5 %, in one of 14 ex. (25<sup>th</sup> June) it was 18.5 %. The length of the coleoptiles varied between 20 and 32 mm.

We are allowed to conclude from this, that the coleoptile still grows at 2 to 3 mm. distance from the top, and that a paraffine cap with a melting point of 38° Cels. does not hinder the growth and is stretched by it.

The increase of distance found here is not as large as the increase of resistance, found by BRAUNER after three hours in the dark. It is, however, of sufficient prominence to make us admit the necessity of a closer investigation of the influence of the distance of electrodes at measurements of resistance like those done by BRAUNER.

As regards the conclusions to be derived from the results of these measurements, we therefore have to count with the possibility that the increase of resistance may contain at least a component, due to the growth; whilst in the diminished increase of resistance under influence of light, a part may be taken by the decrease of growing speed during the first hours. The extent of this part may perhaps be stated by experiment, but anyhow this question has to be counted with, for it might be, by the method followed hitherto, that we should take something to be the cause of the light-growth-response, which partially, even is a result of growth itself.

I thought it desirable to go into the methodical question attached to this matter, too, as even in the nearest future it might occur, that confirmation or contradiction of the theory of BLAAUW will be made dependent — wrongly — on the existing or missing resemblance of curves to the graphs of the light-growth-response.

The investigator, who wishes to test BLAAUW's theory by experiment, should not lose sight of the real contents of this theory. BLAAUW himself (2, p. 171) formulates his explanation of Phototropism: "Wo das Licht eine Wachstumsreaktion hervorruft, ruft eine ungleiche Lichtverteilung ein ungleiches Wachstum hervor, welches wir Phototropismus nennen".

The aim is, therefore, to examine the difference in result of equal and unequal light-distribution around the circumference of the organ. It, consequently, belongs to the task of the investigator, to examine this light-distribution as closely as possible.

The fact that this is sometimes neglected without being counter-balanced by the prudence in conclusion then required, appears from a publication made by two Czechic experimentators ŮLEHLA and MORÁVEK: "On a photo-growth reaction without phototropical curvature" (9).



This title is founded by them on the following experiment:

Top cells of hyphen of the fungus *Basidiobolus ranarum* are observed with the microscope, and, with the aid of a "camera lucida", every two or three minutes the outline of the top is drawn, from which the growing process is noted. The illumination, to which the cells are exposed (either with lightpushes or uninterruptedly) comes from the side through a narrow horizontal slit, so that the light beams pass horizontally between the object-slide and the cover and eventual curvations are not hindered by the glass slides. The cell is then visible in a dark field, whilst (9, p. 124) "the side turned to the slit is sharply outlined, the other side coincides with the interference lines — the hyphen acting as a diffraction grate. Apparently, an important difference of intensity exists here between both sides of the hyphen, in relation to the incident beams. This is a cardinal point, for such a difference in intensity is required by BLAAUW's theory in cases where a phototropical reaction may be expected".

The light intensities used are very high (mostly more than 100.000 Meter Candle) as the fungus shows no reaction otherwise. "For *Basidiobolus*, the light is no ecological factor" (9, p. 123). The authors think this to be of great importance, as they wish to investigate a plant, which has not developed a particular light sensibility, and in which "the processes produced by light ought to be considered rather as simply physico-chemical". (9, p. 124).

The results are summarised by the authors as follows (9, p. 139, 140):

(1) The top cells of *Basidiobolus* do not react on an instantaneous, week illumination; if stronger illuminated, they give the typical photo-growth reaction as described by BLAAUW for the first time.

(2) This reaction is positive up to certain intensity and changes in a negative one at higher intensities<sup>1)</sup>.

[(3 and 4) At the same time changes in the shape are going on, called "photo-formreaction" by the authors].

(5) Although the *Basidiobolus* shows the photo-growth reaction, yet it does not bend itself in the direction of one-sided illumination, neither towards the light, nor from the light; it is therefore not phototropical.

(7) From this fact we assume, that BLAAUW's theory is founded on an established fact, but cannot be true for all cases.

So far the authors. It is as remarkable as it is instructive, that

<sup>1)</sup> From the tables appears, that the words "positive" and "negative" apply to the beginning of the reaction.

the existence of this investigation has reached general attention for a great deal by an abstract, published by P. STARK in the *Zeitschr. f. Bot.* (7) in which, however, only the far-reaching (English) conclusions have been mentioned, and these partially inexactly. The commanding necessity of taking at hand the original publication<sup>1)</sup>, appears from the following considerations:

A. The starting point of the experiments was not the opposition: all-sided illumination produces light-growth-response — one-sided illumination causes curvature. The authors always operated with one-sided illumination, and did find light-growth-response, but no curvature (*although fig. 1 and 3 clearly show curvations, which, however, remain unmentioned*).

B. The authors themselves memorate, that the appearing of a curvature depends on the light distribution round the circumference of the cell inside the cell wall. In their own case, however, they content themselves with stating, that the light, reflected to their eye from the light side, was much more intense than that reflected from the shadow side.

This, of course, does not prove anything about the distribution of the light over the protoplasm. BLAAUW (1, p. 688) wrote on this subject in connection with *Phycomyces*: "Man hüte sich dabei, die starke Reflexion des Lichtes an den Aussenwänden der Zelle ("nitens!") mit der Lichtkonzentration im Inneren der Zelle zu verwechseln".

This shows sufficiently, that the conclusions drawn by the authors, may be called at least premature, and that, in general, when testing BLAAUW's theory on new objects, the question of the internal light distribution requires prominent attention.

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*Amsterdam, September 1924.*

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<sup>1)</sup> For the translation from the Czechic, I am much indebted to Mr. A. E. BOUTELJE.



**Chemistry.** — "*Researches on the Addition of Gaseous Hydrochloric Acid and Hydrobromic Acid to Ethylene and Propylene under the Influence of Catalysts.*" By J. P. WIBAUT, J. J. DIEKMANN, and A. J. RUTGERS. (Communicated by Prof. S. HOOGEWERFF).

(Communicated at the meeting of June 28, 1924).

In this communication further researches are discussed on addition reactions to ethylene and propylene. On the addition of water to these compounds a preliminary communication has already appeared in these Proceedings<sup>1</sup>).

I have been able to carry out this investigation by the aid of a support granted me out of the HOOGEWERFF-fund: for this kindness I express again my heartfelt thanks to the Board of Trustees of the HOOGEWERFF-fund.

The experiments on the addition of hydrochloric acid and hydrobromic acid to ethylene and propylene were undertaken by me in conjunction with Mr. DIEKMANN. When it had already been found that these reactions can be realized by means of the catalysts to be described below, Mr. DIEKMANN was obliged to interrupt this work on account of his military duties. I then continued the investigation in conjunction with Mr. RUTGERS.

The researches described here were already completed for the greater part in September 1923; with a view to the filing of a patent the publication was postponed<sup>2</sup>).

J. P. WIBAUT.

### § 1. *Introduction.*

It is a characteristic property of the olefines that these substances can combine with hydrogen halide. This reaction takes place most readily with hydriodic acid; hydrobromic acid also reacts smoothly in many cases, whereas the addition of hydrochloric acid in general proceeds much more slowly. In general the addition of hydrogen halide to the higher olefines takes place more readily than to the lower terms of the series.

<sup>1</sup>) WIBAUT and DIEKMANN, These Proceedings 26, p. 321—328.

<sup>2</sup>) French patent 574.800; Dutch patent filed on January 12th, 1923; English patent 209.722.

About the addition of hydrogen halide to ethylene an investigation of BERTHELOT<sup>1)</sup> was known when we started our experiments. This investigator heated ethylene with a saturated solution of hydrobromic acid at 100° C. in a sealed glass bulb for 100 hours; ethylbromide was formed. A solution of hydriodic acid reacted somewhat more rapidly under the same circumstances.

If the same experiment was made with ethylene and concentrated hydrochloric acid, only traces of a neutral substance containing chlorine were formed, which could not be identified. From this it appears that the addition of hydrochloric acid to ethylene proceeds very slowly under these circumstances.

If propylene was heated with aqueous hydrochloric acid in the same way at 100°, the hydrochloric acid was completely absorbed after 70 hours with formation of isopropylchloride.

We have set ourselves the task of examining the reaction between gaseous hydrochloric acid and hydrobromic acid and ethylene, resp. propylene. These olefines are now available in great quantities as components of coal gases (coke-oven gas and gases of the coal distillation at low temperature) and in the gases obtained in the preparation of light hydrocarbons from heavy petroleum-distillates (cracking process). Therefore an investigation on the possibility of transforming the ethylene resp. propylene out of these gas mixtures into the corresponding alkylchlorides looked promising, as these alkylchlorides, in particular ethylchloride, find various applications in chemical industry. As will appear from what follows, we have actually attained our end.

In the mean time several investigations have become known bearing on the same problem. In a German patent of the "Farbenfabriken vorm. FR. BAYER and Co." (D. R. P. 361041) it is stated that ethylene and gaseous hydrochloric acid combine to ethyl chloride at temperatures between 200° and 300°, when a mixture of these gases passes over indifferent substances, as fragments of stone, charcoal, pumice, and similar substances; these substances would serve to transmit the heat. Oxides of heavy metals, in particular "roasted pyrites", might serve as catalysts in this reaction. In a patent of the chemical factory WEILER TER MEER (D. R. P. 369702) another method for the preparation of ethylchloride from ethylene and gaseous hydrochloric acid is protected. These substances are pressed in an autoclave filled with charcoal. At 100°—200° and at a pressure

<sup>1)</sup> Compt. r. Acad. d. Sc. 44, 1350; 50, 612.

Lieb. Ann. 104, 184 (1857) en 115, 114 (1860).

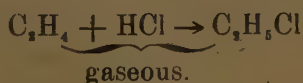


of 25—50 atmospheres ethylchloride is said to be formed in a quantitative yield.

We had already found in our preliminary experiments that when a mixture of ethylene and gaseous hydrochloric acid is passed over asbestos, over granules of burned clay or over charcoal, no formation of ethylchloride takes place between 100° and 270°. This is, therefore, in conflict with the statement of the just-mentioned patent of BAYER. Between gaseous hydrobromic acid and ethylene there appeared to proceed a slow addition reaction at 140°—170° in the presence of asbestos.

If the thermic effect of the formation of ethyl chloride from hydrochloric acid and ethylene is considered, this reaction appears to be strongly exothermic. The heat of combustion of ethyl chloride has been determined by THOMSEN and by BERTHELOT. In the experiments of these two investigators the products of combustion formed were: carbonic acid, liquid water, hydrochloric acid and very little free chlorine. In THOMSEN's experiments part of this hydrochloric acid occurred in the gaseous state. BERTHELOT burned gaseous ethylchloride with oxygen in his calorimetric bomb; the hydrochloric acid gas dissolved in the water, which had been put in the bomb. Both BERTHELOT and THOMSEN have determined the quantity of free chlorine and recalculated the results for the case that only hydrochloric acid should be formed in the combustion; for this calculation the heat of formation of hydrochloric acid and that of water must be known. In the case of ethylchloride this correction is small.

The heat of combustion of ethylene has been determined both by THOMSEN and by BERTHELOT. Hence the heat that is liberated when hydrochloric acid combines with gaseous ethylene can be calculated from these results, provided that the heat of solution of hydrochloric acid in water is taken into account, since in the combustion of ethylchloride an aqueous solution of hydrochloric acid is formed. In this way THOMSEN and BERTHELOT have calculated the thermic effect of the reaction:



BERTHELOT finds for the thermic effect 31,9 cal., THOMSEN gives 10,8 cal. THOMSEN has calculated the heat of reaction at constant volume, whereas BERTHELOT's value is valid for constant pressure, but the ensuing difference is comparatively small. In the combustion of ethylbromide both hydrobromic acid and free bromine is formed in considerable quantity, which rendered the experiments and the

calculation still more complicated. Below we give the values for the heats of reaction of some of these reactions as these values have been given on one side by THOMSEN, on the other side by BERTHELOT.

	THOMSEN <sup>1)</sup>	BERTHELOT <sup>2)</sup>
$C_2H_4 + HCl$	10.84 Cal.	31.9 Cal.
$C_3H_6 + HCl$	11.96 "	
$C_4H_8 + HCl$	12.13 "	
$C_2H_4 + HBr$	12.87 "	29.1 "
$C_3H_6 + HBr$	14.91 "	

It is seen that the values of THOMSEN and of BERTHELOT differ greatly. We shall not enter into a discussion of the question which of these values are reliable, and how great the accuracy should be estimated, which would be very difficult for want of experimental details, but we will only conclude from these data that the addition of halogen hydrogenic acid to olefines is a clearly exothermic reaction.

In virtue of these thermic data it might be expected that the addition of hydrochloric and hydrobromic acid to ethylene and propylene can proceed rapidly enough at the ordinary temperature resp. at a slightly raised temperature, if one has a suitable catalyst at one's disposal. It is natural to look for catalysts for this reaction among the metal chlorides, in order to avoid secondary reactions; for instance when metal oxides are used, the chlorides would be formed from this through the action of hydrochloric acid gas.

In the literature only few data were to be found to decide in which groups of the periodic system one had to find such a catalyst. SABATIER and MAILHE <sup>3)</sup> have studied the decomposition of alkylchlorides and alkylbromides in halogen hydrogenic acid and the corresponding olefine. They found that this reaction is catalytically accelerated by the chlorides of bi-valent metals as  $NiCl_2$ ,  $CoCl_2$ ,  $FeCl_2$ ,  $PbCl_2$ , and  $BaCl_2$ . When ethylchloride or propylchloride is led over barium chloride at  $300^\circ C$ . a smooth decomposition takes place into hydrochloric acid gas and ethylene. The chlorides of sodium potassium or of silver do not promote this reaction according to SABATIER and MAILHE; in the presence of these substances there

<sup>1)</sup> These values are those calculated by THOMSEN from the heats of formation; see *Thermochemische Untersuchungen*, Bd. IV, 372.

<sup>2)</sup> *Annales de Chimie et de Physique* (5), t. 23, 238 (1881).

<sup>3)</sup> *Compt. r. Acad. d. Sc.* 141, 238 (1905).



is no decomposition even at  $350^{\circ}$ . According to SENDERENS<sup>1)</sup> also aluminium oxide, silicium dioxide, aluminium sulphate are catalysts for the splitting off of hydrochloric acid from alkylchlorides. We have tried if barium chloride, which according to SABATIER and MAILHE is the most suitable catalyst for the decomposition of alkylhalides, would act catalytically on the addition of hydrochloric acid to ethylene or propylene, but have not been able to find the slightest influence of barium chloride on this reaction.

GUSTAVSON<sup>2)</sup> has investigated the action of hydrobromic acid on ethylene in the presence of aluminium bromide. This investigator led a mixture of hydrobromic acid gas and ethylene over anhydrous aluminium bromide. At  $60^{\circ}$ — $70^{\circ}$  there took place a vigorous reaction in which, however, a complex reaction product was formed, wherein besides a substance which seemed to be a compound of aluminium bromide with a hydrocarbon, also saturated hydrocarbons occurred. If the reaction was carried out at  $0^{\circ}$ , a pretty large quantity of ethylbromide was formed, according to GUSTAVSON (quantitative data are not given), but even at this temperature other reactions occurred.

As it appeared from GUSTAVSON's experiments, which are not described very clearly, that aluminium bromide causes a complicated reaction process, we have not included this substance in our investigation.

We have found that bismuth trichloride and antimonytrichloride resp. the corresponding bromides are excellent catalysts, which cause the addition of hydrochloric acid and hydrobromic acid to ethylene and propylene to take place rapidly.

Recently a paper has been published by E. BERL and J. BITTER<sup>3)</sup> on the addition of hydrochloric acid gas to ethylene. These investigators used anhydrous aluminium chloride as a catalyst, after it had appeared to them that in an empty glass tube the addition of hydrochloric acid to ethylene does not take place. They find that in the presence of aluminium chloride the addition of hydrochloric acid to ethylene proceeds at temperatures from  $100^{\circ}$  C. upwards; only a small quantity of by-products was formed. These investigators have not carried out experiments with hydrobromic acid, neither with propylene.

## § 2. *Experimental part.*

We have prepared the ethylene required for these experiments according to SENDERENS' method, by conduction of the vapour of

1) Bull. Soc. chim. d. France (4), 3, 823 (1908).

2) Journ. f. prakt. Chemie (2) 34, 161 (1886).

3) Ber. d. deutsch. chem. Ges. 57, 95 (1924).

ethyl alcohol over heated aluminium sulphate. SENDERENS gives a very extensive description of the best way in which the catalyst for this reaction is to be prepared. According to our experience no special care need be taken to obtain a suitable catalyst for this reaction. We have soaked asbestos with a strong solution of aluminium sulphate; the evaporated mass was dried at  $130^{\circ}$  and powdered. With such a catalyst we have obtained excellent results. The best temperature for the reaction was  $370^{\circ}$ — $380^{\circ}$ . The propylene was always prepared from propylalcohol, which is much cheaper than isopropylalcohol, and yields equally good results. The ethylene and propylene obtained in this way, always contains a little hydrogen dependent on the temperature of reaction and the particular properties of the catalyst. Since this quantity of hydrogen had no injurious influence in our experiments, we have not removed the hydrogen, but determined the percentage of olefine of each gas mixture used. In this way, we have indeed often obtained a gas with 99,5 % olefine.

The reaction space consisted of a glass tube of a length of 100 cm. A wire of chromium nickel was wound round this tube immediately on the glass, which wire was connected with the electrical circuit. By means of a suitable resistance any required temperature between  $100^{\circ}$  and  $300^{\circ}$  could be kept constant in the reaction tube. Round the reaction tube a wider glass tube was placed concentric with it, which served for heat-insulation. This electrical furnace has the advantage that the inside of the reaction space can be watched during the experiment. The temperature of the reaction was measured by means of a thermo-element, which was mounted inside the reaction tube. The ethylene came from a graduated glass gasholder, passed through a *U*-tube with calciumchloride, and washing-bottle with strong sulphuric acid, which at the same time served as gas-bubble counter, and then entered the reaction tube. In the experiments with propylene, the washing-bottle was filled with 90 % sulphuric acid. Hydrochloric acid gas was developed from sulphuric acid and ammonium chloride, also passed through a washing-bottle with sulphuric acid, and mixed with the olefine before the reaction space was reached. The proportion between hydrochloric acid gas and olefine was approximately determined by counting the gas bubbles in the washing bottles, which were of the same demensions.

Hydrobromic acid was prepared by leading a mixture of hydrogen and bromine vapour over heated platinum; then the reaction mixture was led through tubes with anthracene in order to remove unchanged bromine vapour. With some practice a pretty constant stream of



hydrobromic acid gas can be obtained in this way, which mixed with the olefine and entered the reaction tube.

The gases issuing from the reaction tube were freed from unchanged hydrogen halide by means of *U*-tubes filled with soda-lime, and then the halogen alkyl was condensed in a convenient way. In the case of ethyl chloride a spiral cooled in carbonic acid and alcohol was required for this. In order to drive all the halogen alkyl present in the reaction tube into the receiver, air was passed through the reaction tube and the *U*-tubes for two hours after the experiment. The *U*-tubes were heated to a suitable temperature in the case of ethylbromide and of the isopropyl halogenides.

The yield of halogen alkyl was measured in most experiments by the weight of the distilled alkyl halide. In our preliminary experiments on the addition of hydrochloric gas we have followed another method. The gas mixture which had been carefully freed from hydrogen halide passed by way of control through a washing bottle filled with a solution of silver nitrate, then through a drying tube, after which it entered a quartz tube heated to redness. There the ethyl chloride or iso-propylchloride was decomposed and hydrochloric acid was split off. The quantity of this was determined by the titration of the chlorine ion. This method has rendered us good services to test the addition of hydrochloric acid during an experiment, especially in the experiments with illuminating gas which will be mentioned later. BERL and BITTER have applied the same method independently of us in the said paper. In the subjoined tables we shall now give a survey of the results, in which only a number of typical experiments are mentioned out of the great number of experiments made.

In the first column is found the number of the experiment; in the 2<sup>nd</sup> column is indicated the contact substance with which the reaction tube was filled; the third column contains the numbers of litres of gas used in the experiment, and the percentage of olefine of this gas mixture; the 4<sup>th</sup> column gives the duration of the experiment; the 5<sup>th</sup> column the temperature. In the 6<sup>th</sup> column the result is recorded and the yield of alkylhalogenide is calculated with respect to the quantity of olefine.

In all the experiments a reaction tube of the same dimensions was used, which was filled over the same length with catalyst or indifferent substance. Accordingly the experiments are comparable inter se. The gas volumes given have been reduced to 0° and 760 mm. These volumes have, however, not been measured accurately; the errors may amount to some percentages, the same uncertainty pre-

vails, therefore, in the values indicating the yield. A greater accuracy in the measurement of the gas volumes was not necessary, as comparatively small differences in the yield are also caused by the oscillations in the velocity of the current of the gas mixture, by differences in the filling of the tube and similar causes, which we could not perfectly control with the arrangement of our experiments.

The differences between the behaviour of ethylene and propylene, of hydrochloric and hydrobromic acid, the characteristic action of catalysts are, however, very evident in these comparatively rough experiments.

In the gas volumes given, the volume of the admixed halogen hydrogen gas is *not* included. In the case of hydrochloric acid gas the volume of this was about 30—50 %, more than the volume of the olefine. In the case of hydrobromic acid gas the quantity of this was more difficult to ascertain. The hydrobromic acid gas was, however, always present in excess. (See the table on the next page).

It appears clearly from table I that bismuth chloride is a specific catalyst for the addition of hydrochloric acid gas to ethylene. Whereas in the presence of indifferent substances as asbestos, charcoal carbon, granules of burned clay, no ethylchloride is formed even at 220°—270°, or at least very little (experiment 92), the reaction takes place slowly already at room temperature in the presence of BiCl<sub>3</sub> (experiment 76); at 120°—200° with bismuth trichloride as a catalyst the reaction takes place pretty rapidly, and a good yield is therefore obtained. The transformation of ethylene in ethylchloride proceeds still smoothly when the ethylene is mixed with a great excess of air, as appears from experiment 142. In this experiment the ethylchloride formed was isolated from the gaseous reaction product through absorption with active charcoal, after unchanged hydrochloric acid had first been removed, and then the ethylchloride had been obtained through distillation from the active charcoal. It has appeared to us that a number of experiments can be performed with the same mass of catalyst, without any decrease of activity being perceptible. (Compare the series of experiments 72—79: this same catalyst was also used in later experiments. Compare table II).

We have often verified the purity of the ethylchloride obtained in these experiments by distillation. The greater part of the reaction product distilled from 12°—12°,8. Except for a little dissolved ethylene, the reaction product seemed to contain no impurities. Substances



which boiled at a higher temperature than ethylchloride were not present in appreciable quantity.

TABLE I. (Ethylene and gaseous hydrogen chloride).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
92	Asbestos	4.2 l. 97 % $C_2H_4$	6	220°	About 0.04 gr. $C_2H_5Cl$ i.e. 0.3 %
93	"Bayer A—Kohle"	3.2 l. 97 % $C_2H_4$	2	220°	No $C_2H_5Cl$ formed
94	Granules of burned clay	3.3 l. 97 % $C_2H_4$	2	270°	" " "
97	Granules of burned clay	3.3 l. 97 % $C_2H_4$	2	250°	" " "
103	Asbestos soaked with $BaCl_2$	2.5 l. 97 % $C_2H_4$	3.5	170°	" " "
72	Asbestos soaked with $BiCl_3$	4.1 l. 99 % $C_2H_4$	5	150°	8.8 gr. $C_2H_5Cl$ = 74.5 %
73	The same catalyst as in 72	1.5 l. 99 % $C_2H_4$	$3\frac{2}{3}$	120°	3.5 gr. $C_2H_5Cl$ = 81 %
76	The same catalyst as in 72	3.8 l. 99 % $C_2H_4$	6	15°	0.65 gr. $C_2H_5Cl$ = 6 %
77	The same catalyst as in 72	2 l. 99 % $C_2H_4$	$4\frac{1}{2}$	120°	4.7 gr. $C_2H_5Cl$ = 84 %
78	The same catalyst as in 72	2.5 l. 95 % $C_2H_4$	5	150°	5.1 gr. $C_2H_5Cl$ = 75 %
79	The same catalyst as in 72	3.8 l. 92 % $C_2H_4$	3	200°	7.4 gr. $C_2H_5Cl$ = 73 %
142	Asbestos soaked with $BiCl_3$	43 l. of a mixture of 9.5 % of $C_2H_4$ and 90.5 % of air	57	200°	8.6 gr. $C_2H_5Cl$ = 73 %

BERL and BITTER obtained yields of ethylchloride of 18—36 % with respect to the ethylene used. The highest yield was 36.7 % at a reaction temperature of 130°. They worked with a mixture of equal volumes of hydrochloric acid gas and ethylene. It is not possible to make a reliable comparison between the catalytic activity of aluminium chloride and bismuth chloride, because the rate at which the gas was flowing and the dimensions of the reaction tube in BERL and BITTER's experiments were different from those in our

experiments. It seems to us that bismuth chloride is a more active catalyst than aluminium chloride. At 120° we have obtained conversions to 84 %; this is a much higher yield than the two investigators mentioned.

The reaction between ethylene and hydrochloric acid is reversible. BERL and BITTER give a calculation of the equilibrium constant:

$$K_p = \frac{PC_2H_4 \cdot PHCl}{PC_2H_5Cl}$$

admitting a value of 14.2 Cal. for the heat of reaction. They have calculated this value for the heat of reaction from the values for the energy of the atomic linkings as they are given by FAJANS and by MARTIN and FUCHS. As we have seen already in the introduction the result of the measurements of the heats of combustion does not give any reliable value for the heat of reaction.

By the aid of NERNST's well-known approximative formula BERL and BITTER have calculated the values of  $K_p$  for some temperatures; they do not state, however, what numerical values they use for this calculation, besides the value for the reaction heat. For 200° C. they find  $K_p = 5,25$ . The equilibrium concentration of ethylchloride which would correspond to this value of  $K_p$ , is, however, much smaller than the quantity of ethylchloride which is formed according to our experiments and according to the experiments by BERL and BITTER themselves.

We shall not enter further into this question, as in this case no great importance can be attached to the calculation of the equilibrium concentrations on account of the uncertainty in the value of the heat of reaction.

It appears from table II that the reaction between propylene and hydrochloric acid gas proceeds smoothly at 150°. However bismuth trichloride appears to be a powerful catalyst. In the presence of this substance a rapid reaction takes place at the ordinary temperature, with notable generation of heat. The formation of isopropyl chloride proceeds rapidly, even when the propylene is mixed with excess of air (experiment 51).

Antimony trichloride acts as catalyst in the same way.

The product formed is chiefly isopropylchloride, as was, indeed, to be expected according to MARKONIKOV's rule for the addition to olefines. The reaction product of experiment 84 was subjected to fractionated distillation at 755 mm. The following quantities were obtained: 8,5 gr. of 32°—35°, 55 gr. of 35°.5—36°.5, and 10 gr. of 36°.5—38°.5.



TABLE II. (Propylene and gaseous hydrogen chloride).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
32	Asbestos soaked with $\text{BiCl}_3$	6.3 l. 99 % $\text{C}_3\text{H}_6$	2	Initial temp. $20^\circ$	Rapid reaction in which the temp. of the catalyst rose to $70^\circ$ : 15.5 gr. of isopropylchloride, boiling-point $36-37^\circ$ . Yield 68 %.
51	Asbestos soaked with $\text{BiCl}_3$	6 l. of a mixture of 18.6% $\text{C}_3\text{H}_6$ and 81.4% air	4	$18^\circ$	About 80 % isopropylchloride formed (determined by titration of the split off hydrochloric acid.)
56	Asbestos soaked with $\text{SbCl}_3$	6.3 l. 98.5% $\text{C}_3\text{H}_6$	$3\frac{3}{4}$	Initial temp. $18^\circ$	Rapid reaction in which the temperature of the catalyst rose to 60 to $70^\circ$ : 14 gr. of isopropylchloride = 70%: almost the whole quantity distilled from $36.4-36^\circ.8$ .
81	Asbestos soaked with $\text{BiCl}_3$ : the same catalyst was already used in the experiments 72—80	11.7 l. 96% $\text{C}_3\text{H}_6$	6	$100^\circ$	31.6 gr. of crude isopropylchloride = 80 %: the greater part distilled from $36-37^\circ$ .
83	The same catalyst as in N <sup>o</sup> . 81	Mixture of 5 l. $\text{C}_3\text{H}_6$ and 12 l. of air	$4\frac{1}{2}$	$80^\circ-100^\circ$	15.5 gr. of crude isopropylchloride = 92 %. The greater part distilled at $35-37^\circ$ .
84	The same catalyst as in N <sup>o</sup> . 81	27.1 l. 96 % $\text{C}_3\text{H}_6$	10	$80^\circ-90^\circ$	82 gr. of crude isopropylchloride = 92%.
106	Pure asbestos	3.1 l. 90 % $\text{C}_3\text{H}_6$	3	$150^\circ$	6.5 gr. of isopropylchloride = 66 %.
107	Pure asbestos	1.9 l. 90 % $\text{C}_3\text{H}_6$	2	$150^\circ$	3.5 gr. of isopropylchloride = 58 %.
109	Asbestos soaked with $\text{BaCl}_2$	1.3 l. 90 % $\text{C}_3\text{H}_6$	1.5	$150^\circ$	2.2 gr. of isopropylchloride = 55 %.

Whether a little propylchloride is still present in this last fraction, has not yet been ascertained. At any rate the quantity of this substance cannot be large. Besides, the reaction product, which was obtained in the experiments with propylene, contained still a very small quantity of a liquid that did not boil at  $100^\circ$ .

It appears from table III that the addition of hydrobromic acid to ethylene in the presence of asbestos proceeds very slowly at  $140^\circ-170^\circ$ , though there is some ethylbromide formed. Accordingly the addition of hydrobromic acid takes place *ceteris paribus*

more readily than the addition of hydrochloric acid (compare N°. 92, 93, 94, 97, 103 of table I). Bismuth tribromide is again a vigorous

TABLE III. (Ethylene and gaseous hydrogen bromide).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
121	Pure asbestos	1.9 l. 90 % $C_2H_4$	2	140°	0.5 gr. $C_2H_5Br$ = 6 %
128	Pure asbestos	3 l. 93 % $C_2H_4$	4	20°	No $C_2H_5Br$ formed
129	Pure asbestos	1.95 l. 93 % $C_2H_4$	2	170°	0.8 gr. $C_2H_5Br$ = 9 %
133	Asbestos soaked with $BiBr_3$	1.2 l. 93 % $C_2H_4$	2½	90°—100°	4.5 gr. $C_2H_5Br$ = 84 %
134	The same catalyst as in 133	1.7 l. 93 % $C_2H_4$	2½	20°	6.6 gr. $C_2H_5Br$ = 84 %
136	The same catalyst as in 133	0.84 l. 93 % $C_2H_4$	2	170°	3.4 gr. $C_2H_5Br$ = 88 %

catalyst for this reaction: in the presence of this substance a pretty rapid reaction takes place already at the ordinary temperature.

TABLE IV. (Propylene and gaseous hydrogen bromide).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
30	Glass wool on which $BiBr_3$	7.4 l. 96 % $C_3H_6$	2	Initial temp. 20°	34.6 gr. of crude isopropylbromide = 89 %. 30 gr. of this distilled from 59°—60°. The temp. rose during the experiment to 40° C.
122	Pure asbestos	2.4 l. 96 % $C_3H_6$	4	170°	7 gr. of isopropylbromide = 55%. The greater part distilled at 60°
126	Pure asbestos	2.0 l. 96 % $C_3H_6$	2	170°	5.7 gr. of isopropylbromide = 55%
125	Pure asbestos	2.6 l. 96 % $C_3H_6$	3½	20°	8.6 gr. of isopropylbromide = 61%. The greater part distilled at 60°
139	Asbestos soaked with $BiBr_3$	1.9 l. 96 % $C_3H_6$	½	20°	8.7 gr. of isopropylbromide = 93%. The temp. rose to 80° C. at the spot where the mixture of propylene and $HBr$ struck the catalyst



The reaction product from the experiments 129, 134, and 136 was fractionally distilled; the greater part went over from  $38^{\circ}$ — $40^{\circ}$ . There was left only a very small residue. The product is, therefore, almost pure ethyl bromide.

It appears from table IV that the addition of hydrobromic acid to propylene proceeds already pretty rapidly at  $20^{\circ}$  in the presence of asbestos. In the presence of bismuth tribromide, the velocity of the reaction becomes, however, much greater, as appears from the experiments 30 and 139; in these experiments the propylene flowed at a rate of 4 litres per hour, and round 90 % of isopropylbromide could be obtained from this, whereas in experiment 125 with a rate of flow of about, 0.7 L. of propylene per hour, the yield was only 61 %.

### § 3. *Summary of the Results.*

We can give the following summary of these results. The addition of hydrogen chloride to ethylene does not take place between  $170^{\circ}$  and  $270^{\circ}$  without catalyst or, if it does, the velocity of the reaction is very small; in the presence of bismuth chloride, on the other hand, a perceptible reaction takes already place at the ordinary temperature; between  $120^{\circ}$  and  $200^{\circ}$  the reaction proceeds rapidly in the presence of  $\text{BiCl}_3$ , and without formation of by-products. The addition of hydrogen bromide to ethylene proceeds somewhat more readily than the addition of hydrogen chloride. Yet in the absence of a catalyst no addition takes place at  $20^{\circ}$  under the circumstances of the experiment; this reaction does not become perceptible until the neighbourhood of  $140^{\circ}$  is reached. In the presence of bismuth bromide however the reaction proceeds rapidly even at  $20^{\circ}$  C.

The addition of hydrogen halide to propylene takes place much more quickly than that to ethylene, which is apparent both in the addition of hydrogen chloride and of hydrogen bromide. Under the circumstances of these experiments the reaction evidently takes place much more rapidly than in the experiments of BERTHELOT, who worked with an aqueous solution of hydrochloric acid.

Hydrogen bromide appears to react with propylene at lower temperatures than hydrogen chloride. Bismuth trichloride or antimony trichloride resp. bismuth tribromide are powerful catalysts for the reaction between propylene and hydrogen chloride resp. hydrogen bromide; in presence of these substances the reaction proceeds rapidly at the ordinary temperature, while much heat is liberated.

Some interesting questions arise, among others whether in this

reaction there is formed any *n*-propylchloride, resp. *n*-propylbromide, and whether the quantity of this varies with the temperature. From the experiments of table II and IV it appears that chiefly isopropylchloride is formed both at 20° and at 100°, resp. chiefly isopropylbromide at 20° and 170°, but it might perhaps be worth while investigating this point more closely. It will probably be possible to investigate the equilibrium of the reaction:



at very divergent temperatures, now that a vigorous catalyst is at our disposal.

Another question is whether hydrogen halide might be added to aromatic hydrocarbons in this way. Ethylene combines with hydrogen to ethane under the influence of finely divided nickel or platinum, while under the same circumstances cyclohexane is formed from benzene. Would it now be possible that e.g. tribromcyclohexane is formed from benzene vapour and gaseous hydrogen bromide under the influence of bismuth bromide?

Preliminary experiments in this direction with toluene, which is somewhat more easily accessible to addition reactions than benzene, have yielded negative results. We have not been able to find an indication of an addition of hydrobromic acid.

We have finally also made some orientating experiments on the addition of hydrochloric acid gas to acetylene in the presence of bismuth chloride. We have, however, not yet succeeded in realizing this reaction.

#### § 4. *Preparation of Ethyl chloride from Coal-gas.*

We have applied the method found by us to convert the ethylene present in illuminating gas in small quantities, into ethylchloride. We shall not give a detailed description of these experiments, as they do not open any essential new points of view. What *has* appeared from them is, that this reaction can be successfully applied to gas mixtures with a small ethylene-content. The Amsterdam illuminating gas used by us contained<sup>1)</sup> from 1 to 1,8 % of ethylene.

The illuminating gas was first freed from benzene vapour by washing with creosote oil, then passed through a gas-meter and drying-tubes, after which it was mixed with a small quantity of hydrochloric acid gas. The mixture of illuminating gas and hydro-

<sup>1)</sup> Determined by absorption with fuming sulphuric acid in the gas that had previously been freed from benzene vapour. Hence also other olefines are included in this: the quantity of them is, however, very small in illuminating gas.



chloric acid gas was conducted over the bismuth trichloride catalyst between 150° and 200° C. The apparatus was arranged in such a way that the experiment could be continued day and night, without interruption and required little supervision. The ethylchloride formed, which was present only in small concentration in the issuing gas mixture, was isolated by absorption with active charcoal, after the hydrogen chloride that was still present, had been removed. The chief constituents of the illuminating gas were not adsorbed by the charcoal, and left the adsorption-apparatus unchanged. In order to be able to verify in the course of the experiments, whether the charcoal still adsorbed ethylchloride, resp. whether ethylchloride was still being formed in the reaction tube, we made use of the method of analysis mentioned in the beginning, which is based on the splitting off of hydrochloric acid from ethylchloride. From the active charcoal we liberated the adsorbed ethylchloride by heating, and then condensed it by cooling.

In the paper cited, BERL and BITTER have also applied the adsorption of ethylchloride by means of active charcoal.

To give an example we obtained 5,8 gr. of pure ethylchloride from 360 litres of illuminating gas, which quite distilled over from a water bath of 15° C., besides a very small quantity of higher-boiling alkyl chlorides. This corresponded to about 50 % of the quantity of ethylene present in the illuminating gas.

We have also mixed illuminating gas with a little propylene, and obtained a very good yield of isopropyl chloride from this in the same way.

It is of importance that prolonged experiments were made with the same catalyst without this decreasing in activity.

*Organic-Chemical Laboratory of the University.*

*Amsterdam, June 1924.*

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**Mathematics.** — “On Generalisations of the Notion of Absolute Convergence”. By M. J. BELINFANTE. (Communicated by Prof. L. E. J. BROUWER.)

(Communicated at the meeting of March 29, 1924).

In an article, entitled: “Sur la sommabilité absolue des séries par les moyennes arithmétiques” <sup>1)</sup> KOGBETLIANTZ has extended the notion of absolute convergence to summable series, and has proved some theorems concerning this so-called “absolute summability”, which theorems are generalisations of the well known theorems of CAUCHY and MERTENS about the product of two infinite series.

If we substitute the words “joinable of order  $p$ ” instead of “summable of order  $p$ ” in these theorems of KOGBETLIANTZ, then we get generalisations of the theorems of CAUCHY and MERTENS, which I have proved in the articles “A Generalisation of MERTENS’ Theorem” <sup>2)</sup>, “On the Product and Summability of Infinite Series” <sup>3)</sup> and my dissertation <sup>4)</sup>. This may be seen from the following scheme:

*Theorems I. The product of a series which is  $\frac{\text{absolutely summable}}{\text{joinable}}$  of order  $p$ , by a series which is  $\frac{\text{absolutely summable}}{\text{joinable}}$  of order  $q$ , is  $\frac{\text{absolutely summable}}{\text{joinable}}$  of order  $p + q$  <sup>5)</sup>.*

*Theorems II. The product of a series which is  $\frac{\text{absolutely summable}}{\text{joinable}}$  of order  $p$ , by a series, which is summable of order  $q$ , is summable of order  $p + q$  <sup>6)</sup>.*

The theorems I are generalisations of CAUCHY’s theorem to which both are reduced if we take  $p = 0$ ,  $q = 0$ ; the theorems II are generalisations of MERTENS’ theorem to which both are reduced if we take  $p = 0$ ,  $q = 0$ .

<sup>1)</sup> Comptes Rendus de l’Académie des Sciences, t. 178, p. 295—298; 1924.

<sup>2)</sup> These Proceedings. Vol. 26, p. 203—215. The article will be cited as “Art Mert”.

<sup>3)</sup> These Proceedings, Vol. 27, p. 33—45.

<sup>4)</sup> „Over oneindige reeksen”. Noordhoff, Groningen 1923. p. 22—31.

<sup>5)</sup> KOGBETLIANTZ, l. c. p. 297 theorem IV.

„Over oneindige reeksen”, p. 30 theorem 8.

<sup>6)</sup> KOGBETLIANTZ, l. c. p. 297 theorem V.

„Art. Mert.”, p. 204.



We now will prove that the notions of absolute summability and joinability are not equivalent, and that series exist, which are absolutely summable of order  $p$  but not joinable of order  $p$  and also series which are joinable of order  $p$  but not absolutely summable of order  $p$ .

A series is joinable of order  $p$  ( $p > 0$ ) if it is summable of order  $p$  and its mean-values of order  $p - 1$  are finite, or in other words: if it is summable  $(C, p)$  and finite  $(C, p - 1)$ . A series is joinable of order zero if it converges absolutely.

A series  $\sum a_n$  is absolutely summable of order  $p$  if the series of differences of two immediately following mean-values  $\frac{S_n^{(p+1)}}{A_n^{(p+1)}}$  of order  $p$  converges absolutely, i.e. if the series

$$\sum_{1}^{\infty} \left\{ \frac{S_n^{(p+1)}}{A_n^{(p+1)}} - \frac{S_{n-1}^{(p+1)}}{A_{n-1}^{(p+1)}} \right\}$$

converges absolutely <sup>1)</sup>.

In order to find out whether the defined properties are dependent from each other, we reduce the  $n^{\text{th}}$  term  $u_n^{(p)}$  of the above series as follows:

$$\begin{aligned} u_n^{(p)} &= \frac{S_n^{(p+1)}}{A_n^{(p+1)}} - \frac{S_{n-1}^{(p+1)}}{A_{n-1}^{(p+1)}} = \frac{A_{n-1}^{(p+1)} S_n^{(p+1)} - A_n^{(p+1)} S_{n-1}^{(p+1)}}{A_n^{(p+1)} A_{n-1}^{(p+1)}} \\ &= \frac{A_{n-1}^{(p+1)} S_n^{(p+1)} - A_{n-1}^{(p+1)} S_{n-1}^{(p+1)} + A_{n-1}^{(p+1)} S_{n-1}^{(p+1)} - A_n^{(p+1)} S_{n-1}^{(p+1)}}{A_n^{(p+1)} A_{n-1}^{(p+1)}} \\ &= \frac{A_{n-1}^{(p+1)} [S_n^{(p+1)} - S_{n-1}^{(p+1)}] - S_{n-1}^{(p+1)} [A_n^{(p+1)} - A_{n-1}^{(p+1)}]}{A_n^{(p+1)} A_{n-1}^{(p+1)}} \\ &= \frac{A_{n-1}^{(p+1)} S_n^{(p)} - S_{n-1}^{(p+1)} A_n^{(p)}}{A_n^{(p+1)} A_{n-1}^{(p+1)}} \\ &= \frac{A_n^{(p)}}{A_n^{(p+1)}} \left\{ \frac{S_n^{(p)}}{A_n^{(p)}} - \frac{S_{n-1}^{(p+1)}}{A_{n-1}^{(p+1)}} \right\} \\ &= \frac{p}{p+n-1} \left\{ \frac{S_n^{(p)}}{A_n^{(p)}} - \frac{S_{n-1}^{(p+1)}}{A_{n-1}^{(p+1)}} \right\} \dots \dots \dots (1) \end{aligned}$$

<sup>1)</sup> For the notation see these Proceedings, Vol. 27, p. 34.



$|nu_n| < k$  (which characterize the difference between the notions of absolute summability and joinability) are sufficient to secure the convergence of the product of an arbitrary number of series, provided one of the two properties is valid for each of them <sup>1)</sup>.

If a series  $\sum u_n^{(p)}$  is arbitrarily given, it is possible to calculate the corresponding series  $\sum a_n$  with the aid of the formulas of our previous article; therefore the examples above give after this calculation examples of series, which are absolutely summable but not joinable, respectively of series which are joinable but not absolutely summable of the same order. We also see that series of the last kind may have a less complicated character than those of the first kind: so the series  $1 - 1 + 1 - \dots$  is joinable of the first order but not absolutely summable of the first order <sup>2)</sup>. That the product of this series by a series which is summable of order  $p$  is summable of order  $p + 1$  cannot be proved with the aid of KOGBETLIANTZ' generalisation of MERTENS' theorem, <sup>3)</sup> but follows immediately from the fact that it is joinable <sup>4)</sup> (see theorem II).

Another very important property which also often enables us to reduce the order of summability to a lower degree than that which is given by CESARO'S <sup>5)</sup> rule, is the so-called index of summability which has been introduced by CHAPMAN <sup>6)</sup>. A series which is summable of order  $x$  whatever be  $x > p$  has an index of summability which is equal to  $p$  when it is not summable of any order  $< p$  (the series may or may not be summable of order  $p$ ). On a former occasion <sup>7)</sup>, we have observed that sometimes the theorems concerning the joinability give more information than CHAPMAN'S rule that the index of the product of two series cannot exceed the sum of the indices of the series by more than unity.

Since a series, whose index is equal to  $p$  is certainly summable of order  $p + 1$ , the question arises whether there is some connection between the absolute summability, respectively the joinability of order  $p + 1$  and the index  $p$ . It may be seen from the following examples that these properties do not follow from each other.

1. *Example of a series with an index  $p$  which is not absolutely summable of order  $p + 1$ .*

<sup>1)</sup> Proc. Lond. Math. Soc., Ser. 2, Vol. 11, 1913 (p. 464).

<sup>2)</sup> KOGBETLIANTZ, l. c. p. 296.

<sup>3)</sup> KOGBETLIANTZ, l. c. p. 297.

<sup>4)</sup> „Art. Mert.” p. 211.

<sup>5)</sup> Sur la multiplication des séries. Bulletin des Sciences Mathématiques, 2e série, t. 14, p. 114–120.

<sup>6)</sup> Proc. Lond. Math. Soc., Ser. 2, Vol. 9, p. 369–409, 1911.

<sup>7)</sup> „Art. Mert.” p. 211.



The series  $1 - 1 + 1 - 1 + \dots$  has an index <sup>1)</sup> zero, but is not absolutely summable of order 1.

2. *Example of a series which is absolutely summable of order  $p + 1$ , but whose index exceeds  $p$ .*

The series

$$2 - 1 + 1 - \frac{3}{4} + 0 + 0 + \frac{8}{9} - \dots + 0 + \frac{2r}{r^2} - \frac{2r-1}{r^2} + \underbrace{0 + \dots + 0}_{2r-2 \text{ zeros}} + \frac{2r+1}{(r+1)^2} + \dots$$

is, as mentioned by KOGNETLIANTZ without proof, absolutely summable of the first order but not summable of any order  $< 1$ ; the index therefore exceeds 0.

3. *Example of a series whose index is  $p$ , but which is not joinable of order  $p + 1$ .*

The series

$$1 - \left[ 1 + \frac{1}{2} \right] + \left[ 1 + \frac{1}{2} + \frac{1}{3} \right] - \left[ 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} \right] + \dots$$

has an index equal to zero; indeed it is the product-series of

$$1 - 1 + 1 - 1 + \dots \text{ and } 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

which have the indices 0 and  $-1$  respectively <sup>2)</sup>; hence the index of the product does not exceed  $0 - 1 + 1 = 0$ , and since the series does not converge the index must be 0. The series is not joinable of order 1, since the partial sums:

$$1, -\frac{1}{2}, 1 + \frac{1}{3}, -\frac{1}{2} - \frac{1}{4}, 1 + \frac{1}{3} + \frac{1}{5}, \dots$$

grow infinite.

I have not found an example of a series which is joinable of order  $p + 1$ , but whose index would exceed  $p$ . Hence it might occur that each series which is joinable of order  $p + 1$  would have an index not less than  $p$ .

We will now give a condition which when satisfied for a series with an index  $p$  guarantees that the series is joinable of order  $p + 1$ .

That the index of the series  $\sum a_n$  is  $p$ , is expressed by the following relation:

$$\lim_{n \rightarrow \infty} C_n^{(p+i)} = s \quad \dots \quad (3)$$

if  $i > 0$ .

( $C_n^{(k)}$  is the  $n^{\text{th}}$  mean-value of order  $k$ ).

<sup>1)</sup> CHAPMAN, l. c., p. 378.

<sup>2)</sup> Proc. Lond. Math. Soc., Ser. 2, Vol. 11, p. 462, 1913.

It is not allowed to infer from the existence of (3) that there exists a number  $M$  such that:

$$|C_n^{(p+i)}| < M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for  $i > 0$ . (In that case we call the mean-values of order  $p + i$  uniformly limited for  $i > 0$ ).

Indeed, although it is possible to calculate a number  $M_i$  for every  $i > 0$  such that (4) is satisfied, it might happen that the values of  $M_i$  could increase to  $\infty$  with decreasing  $i$ . It will be seen that this is the case with the series of example (3).

We now prove that if the relation (4) is satisfied whatever be  $i > 0$ , it is also satisfied for  $i = 0$  if  $M$  is replaced by another finite number  $M'$ , i.e. we prove that it is possible to calculate a finite number  $M'$  so that

$$|C_n^{(p)}| < M' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

whatever be  $n$ , which implies that  $\sum a_n$  is joinable of order  $p + 1$ .

To prove this property (which is not self-evident), we introduce the quantities  $A_n^{(-k)}$  for  $0 < k < 1$  by the following definitions:

$$\left. \begin{aligned} A_1^{(-p)} A_1^{(p)} &= 1 \\ A_n^{(-p)} A_1^{(p)} + A_{n-1}^{(-p)} A_2^{(p)} + \dots + A_1^{(-p)} A_n^{(p)} &= 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (I)$$

The quantities  $A$  with negative upper-indices satisfy the same kind of relations as the  $A$ 's with positive indices. In particular we have:

$$A_1^{(p+i)} A_n^{(-i)} + A_2^{(p+i)} A_{n-1}^{(-i)} + \dots + A_n^{(p+i)} A_1^{(-i)} = A_n^{(p)} \quad . \quad (II)$$

$$S_1^{(p+i)} A_n^{(-i)} + S_2^{(p+i)} A_{n-1}^{(-i)} + \dots + S_n^{(p+i)} A_1^{(-i)} = S_n^{(p)} \quad . \quad (III)$$

$$\left. \begin{aligned} A_1^{(-p)} &= 1 \\ A_n^{(-p)} &= \frac{(-p) \cdot (-p+1) \cdot \dots \cdot (-p+n-2)}{1 \cdot 2 \cdot \dots \cdot (n-1)} \end{aligned} \right\} \quad . \quad . \quad (IV)$$

These relations are proved by induction from the definitions (I) and the formulas for positive indices<sup>1)</sup>. From (IV) it is evident that the  $A$ 's with negative upper-indices are all negative except  $A_1^{(-p)}$ .

$$\text{Now, if } |C_n^{(p+i-1)}| < M \text{ or } \left| \frac{S_n^{(p+i)}}{A_n^{(p+i)}} \right| < M$$

whatever be  $n$ , then it follows from (III):

<sup>1)</sup> These Proceedings, Vol. 27, p. 34.

$$\begin{aligned}
|S_n^{(p)}| &< |S_1^{(p+i)} A_n^{(-i)} + S_2^{(p+i)} A_{n-1}^{(-i)} + \dots + S_{n-1}^{(p+i)} A_2^{(-i)}| + |S_n^{(p+i)} A_1^{(-i)}| \\
&< M |A_1^{(p+i)} A_n^{(-i)} + \dots + A_{n-1}^{(p+i)} A_2^{(-i)}| + M A_n^{(p+i)} \\
&< M |A_1^{(p+i)} A_n^{(-i)} + \dots + A_n^{(p+i)} A_1^{(-i)} - A_n^{(p+i)} A_1^{(-i)}| + M A_n^{(p+1)} \\
&< M |A_n^{(p)} - A_n^{(p+i)}| + M A_n^{(p+i)} \\
&< M A_n^{(p)} + 2 M A_n^{(p+i)} \\
\left| \frac{S_n^{(p)}}{A_n^{(p)}} \right| &< M + 2 M \frac{A_n^{(p+i)}}{A_n^{(p)}}.
\end{aligned}$$

Since this relation is valid whatever be  $i$ , we may take  $i$  for a given  $n$  so that  $\frac{A_n^{(p+i)}}{A_n^{(p)}} < 2$ . Indeed

$$\frac{A_n^{(p+i)}}{A_n^{(p)}} = \left(1 + \frac{i}{p}\right) \left(1 + \frac{i}{p+1}\right) \dots \left(1 + \frac{i}{p+n-2}\right) < \left(1 + \frac{i}{p}\right)^n.$$

So, if we take  $i$  less than  $p(\sqrt[n]{2}-1)$  we have  $\frac{A_n^{(p+i)}}{A_n^{(p)}} < 2$ . Hence

$$\left| \frac{S_n^{(p)}}{A_n^{(p)}} \right| < 5M \text{ or } |C_n^{(p-1)}| < 5M \text{ whatever be } n.$$

We have proved that a series which is summable of order  $p$  and whose mean-values of order  $p-1+i$  are uniformly limited for  $i > 0$  is joinable of order  $p$ . If the index of the series is  $p-1$ , then the mean-values are limited for  $i > 0$  but need not be uniformly limited. A sufficient condition that a series with index  $p-1$  shall be joinable of order  $p$  is the condition that the mean-values of order  $p+i-1$  are uniformly limited for  $i > 0$ . As the series of example 3 had an index 0 but was not joinable of order 1, it is clear that we cannot infer from the fact that the index is  $p$  that the mean-values of order  $p+i$  are uniformly limited for  $i > 0$ .

*Note to the article "On the Product and Summability of Infinite Series." (These Proceedings, Vol. 27 p. 33—45).*

The formulas (3) and (5) on page 34 may only be deduced from the formulas (A) and (B) on page 35 if  $p$  or  $q$  or one of them are integer. If  $p$  and  $q$  are not integer then the proof cannot be given in that way; then however the proof is superfluous, as the equality of coefficients has already been inferred from the former case. See my dissertation p. 6.



**Zoology.** — “*Some notes on the Thyroid-metamorphosis in tadpoles*”.

By G. C. HERINGA M. D. (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of June 28, 1924).

Two articles on this subject which appeared in the Arch. für Mikroskopische Anatomie und Entwicklungsmechanik Bd. 101. Heft 1—3, 1924<sup>1)</sup> induce me to refer in this publication to a paper on the same subject, read by me at the meeting of anatomists at Amsterdam in 1923.

It is a long established fact that the influence of thyroid feeding differs largely for the different parts of the body of laboratory animals (larvae). The immediate consequence of this unequal influence is that the larvae coming out from the experiment present a queer combination of tissues and organs in absolute heterogeneous stages of development. Some time ago I endeavoured to describe this peculiar phenomenon as a “dissociation of the developmental process”, which is less conspicuous macroscopically than when the larvae are examined under the microscope. Microscopically it may be best demonstrated by making a comparison between a laboratory -and a control-animal, of which one special organ has reached the same stage of development. So in figs. 1a and 1b two animals are represented of which the small white buds of their still undeveloped hindextremities are equally developed, the former by a thyroid-diet (“Prana”) of some days, the latter in the natural way of gradual development. By immersion into cedar-oil the internal organs have been made visible. In this case the laboratory animal accidentally displays the abrupt shortening of the tail much less than is commonly the case. Besides the great difference in external proportions the amazing difference in the internal structure is very conspicuous: also the almost total disappearance of the gills, the development of the heart, the transformation of the tractus gastro-intestinalis etc. Apart from the rapidity of the metamorphosis

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<sup>1)</sup> W. SCHULTZE, Weitere Untersuchungen über die Wirkung in kretorischer Drüsen Substanzen auf die Morphogenie III. Ueber die Sprengung der Harmonie der Entwicklung. — BENNO ROMEIS, Histol. Untersuchung zur Analogie der Wirkung der Schilddrüsenfütterung auf Froschlarven 2 Die Beeinflussung der Entw. der vorderen Extremität u.s.w.

as a whole, it is evident that a local slowing down in the transformation is to be noted which might readily be interpreted by a different sensitiveness in the various organs. With some degree of reason both SCHULTZE and ROMEIS now expected to be able to determine the point of attachment of the thyroid and therefore they started their investigations from this phenomenon, which SCHULTZE happily proposed to term "*Sprengung der Entwicklungsharmonie*". The conclusions of the authors mentioned, however, are widely diverging.



Fig. 1a.



Fig. 1b.

SCHULTZE's conclusion is in my opinion the less correct of the two. He advances the theory that the epithelial and not the mesodermal tissues have been stimulated to grow. ROMEIS' and my own investigation have produced plenty of data to disprove SCHULTZE's theory. But why should we indicate the weak points in a theory, that sounds like an anachronism in a time when SPEMANN and his followers are completely experimenting down the dogma of the specificity of the germ layers.

We rather advert to the work of ROMEIS, which opens far wider prospects. ROMEIS, who in his histological inquiry confines himself

almost exclusively to the development of the foreleg, immediately emphasizes several important facts<sup>1)</sup>: 1<sup>st</sup>. the significance of the watersecretion as regulated by the thyroids for the general growth: 2<sup>d</sup>. the promoting of cell-division in "definitive organs ("wie z. B. den Extremitäten"), the decomposition of other organs, e. g. the operculum: 3<sup>d</sup>. The significance of the quantity of the supplied thyroid and the time of feeding, f. i. after a certain time it appears that the phenomena of hyperthyroidism give place to those of hypothyroidism<sup>2)</sup>, that anyhow the organs that were precocious at first, afterwards lay behind the organs of the control animal. In short ROMEIS has succeeded in detecting a number of factors which are doubtlessly of consequence for the complicated proceedings. Still there remains a number of phenomena of which ROMEIS utterly fails to give an adequate explanation. Surely, ROMEIS himself thought so too, as he points on the one hand to the complicating interaction of the organs with internal secretion, whose equilibrium is disturbed by the experiment, and on the other hand to the necessity of making allowance for the interaction of the tissues themselves.

But even these restrictions cannot induce us to support ROMEIS' point of view. It is by no means the observations themselves that I want to call in question. The increased diuresis, the augmented mitoses, they are ascertained facts, but in my opinion they do not explain the thyroid-metamorphosis. It seems impossible to me to *explain* the growth of an organism by counting up the number of nuclear cell-divisions. Does it make any difference whether the growth of an extremity-bud is observed macroscopically or whether the numerical increase of the cells is watched under the microscope? The mitoses are so many phenomena of the progressing process, but the process itself remains puzzling as the normal development itself.

This theoretical objection appears to be the more cogent, as we are continually confronted with phenomena which present such a medley of regeneration and degeneration, of differentiation and dedifferentiation, that ROMEIS' arrangement would come to a mere rough-and-ready schematism. Now it goes without saying that so eminent a researcher as ROMEIS has understood this difficulty as, indeed, appears from the above. And yet, he seems not to have entirely escaped the danger of this systematizing. When he considers the accelerated development of an extremity almost exclusively as an increased

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<sup>1)</sup> See also the previous communication by the same author, A. M. A. und E. Vol. 98, 1923.

<sup>2)</sup> It seems plausible to ascribe this fact, which I also observed, to exhaustion.



"Aufbau" in his latest publication, I cannot help asking whether the action of the osteoclasts and the bone-resorption during the growth is to be considered as "Auf-" or as "Abbau".

It is beyond doubt that both, development and demolition, may be brought about by thyroid-action. In this sense ROMEIS' view means a step in advance, as compared with the theory propounded by JARVISCH, who supposes the development to be merely secondary to the decomposition of the larval organs. I am doubtful however, whether it is right to assume evolution in the one region and devolution in the other to be independent parallel processes.

I may be allowed to describe here an observation on the gill-reduction brought about by thyroid, which I have not found mentioned anywhere in the literature. The roof, resp. the posterior wall of the mouth-cavity and the pharynx of normal larvae has a cylindrical epithelium, differentiated by a number of well-defined, small cone-shaped prominences, formed by groups of still considerable higher mucilaginous vacuolated cells. (Fig. 2 and 3). Whether, as I suspect, a glandular function is to be assigned to these cells, or whether they may be buds of a sense-organ is still a matter of

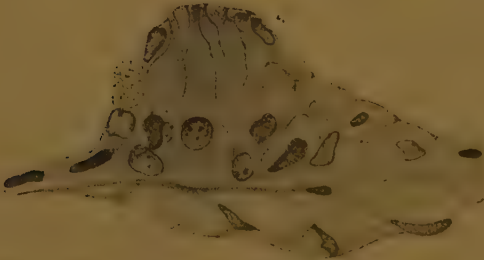


Fig. 2.

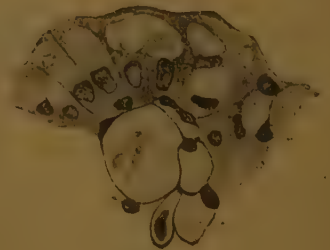


Fig. 3.

conjecture. In the literature I could find only one reference to similar formations and that in a thesis by F. P. SCHULTZE, who describes them as "ein reich entwickeltes System mehrzelliger Drüsen". In some details however his description clashes with my preparations.

Another very remarkable modification of the epithelium to which SCHULTZE (l. c.) also calls attention is found in the roof of the cavity of the gill, extending more or less over the gill-arches. I would not venture to side without further consideration with SCHULTZE, when he concludes that this modification is equivalent to the isolated epithelium-prominences in the mouthcavity. It is certain however, that we here have to do with a high degree of epithelium-modification with a specific function which is very

conspicuous in the section, owing to its high type and great affinity to stains. (Fig. 4 and 5).



Fig. 4. 1)

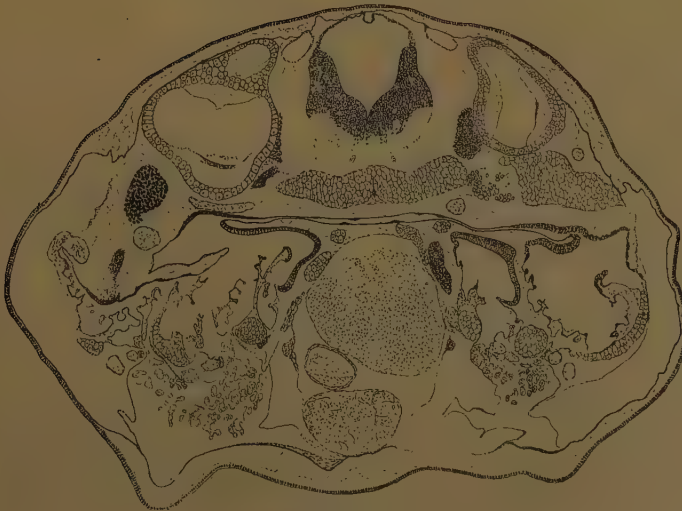


Fig. 5. 1)

1) Figs. 4 and 5. Sections of normal embryos.

Strange to say, this formation again I never found recorded in the literature, although it was represented e. g. in the pictures for a different purpose illustrating the article by EISINGER and STERNBERG (*Arch. für Mikrosk. Anat. Bd. 100*).

Now it is noteworthy that together with the reduction of the gills all these peculiar epithelium formations disappear as it were abruptly after thyroid-feeding (Figs. 6 and 7). From this it may be

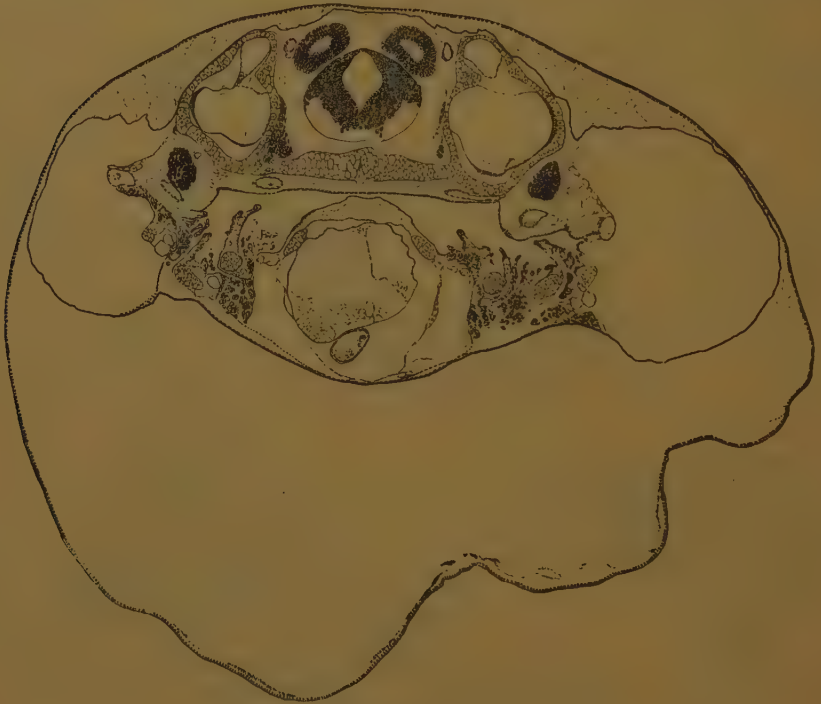


Fig. 6. <sup>1)</sup>

concluded that there is a functional connection with the gill-respiration. Be this as it may, the above affords us a plain instance of the destructive action of the thyroid upon a larval organ. Still here also a more exact analysis gives scope for objections. Is not the blood-vascular system of the gills a highly integral part of the gill apparatus? And is not the definitive apparatus built up from the larval vessels? Several more questions may be asked and all of them will ultimately culminate in the one question: What are "definitive" organs that have been built up, what are larval organs that have been destroyed? Where is the boundary between evolu-

<sup>1)</sup> Figs. 6 and 7. Sections of thyreoidlarvae. Figs. 4—7 all hit the ganglion N. Vagi-Atrophy of the gills.



tion and devolution? Are they not after all two phases of the same process?

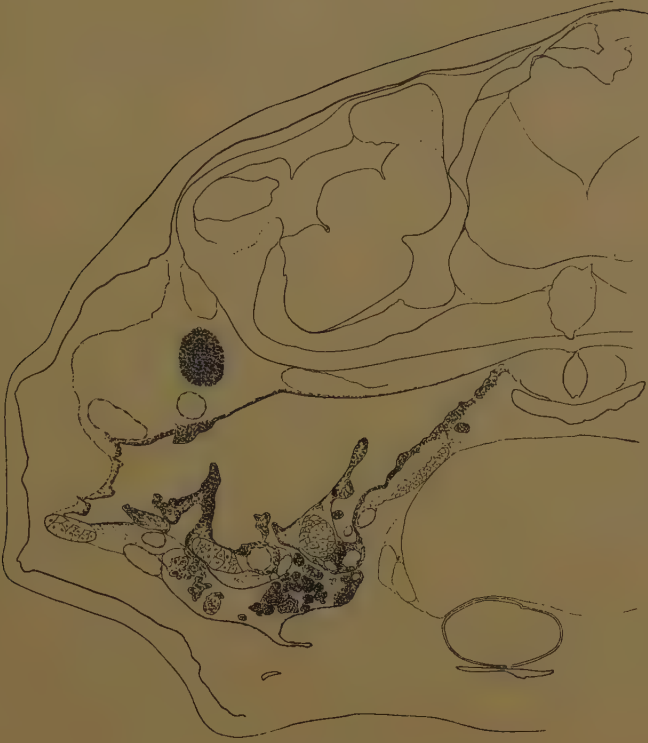


Fig. 7.

Here I think lies the inadequacy of ROMEIS' theory. It seems to me however that our actual knowledge of the whole complicated evolution is still too fragmentary for a deeper analysis. In my opinion the only admissible conclusion is that the thyroid disturbs the equilibrium of the normal progression of the process, nothing else.

In its generality this statement may give little satisfaction but in my judgment it will not be amiss from this point of view once more to define the normal ontogeny as an equilibrated system. In this connection WALTER's experiments should be remembered which demonstrated that after thyroidectomy there appeared neither degeneration nor regeneration of a severed nerve. This is not surprising if we reflect that degeneration is nothing but the introduction to (or the stimulant to) regeneration, as has already been observed by VAN GEHUCHTEN, and as has so conclusively been proved in BOEKE's work. Therefore let us no more set up antitheses between generation and degeneration in ontogeny. Rather let us try to find an explanation for the thyroid action in the shifting of an equilibrium

in local influences, that for the present cannot be defined (let alone localized!). When looking at the facts in this way we shall be amazed at the mysterious agency (entelechy, mneme) that is at work under such an enormous commotion, in keeping together the widely diverged organs and in restoring their development to the normal equilibrium.

*Utrecht, June 24, 1924.*

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**Chemistry.** — “*Equilibria in systems in which phases, separated by a semipermeable membrane.*” I. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of September 27, 1924).

We take a liquid  $L$  of the composition:

$$x \text{ Mol } X + y \text{ Mol } Y + z \text{ Mol } Z + \dots + (1-x-y-z\dots) \text{ Mol } W. \quad (1)$$

and a liquid  $L_0$ , which only contains the simple substance  $W$  (f.i. water). We imagine both liquids, separated from one another by a semipermeable membrane, which allows to pass freely the substance  $W$  only. We call  $W$  the diffusing substance,  $X Y Z \dots$  the not-diffusing substances. Further we assume that  $L$  and  $L_0$  have the same temperature, but that  $L$  is under an external pressure  $P$  and  $L_0$  under an external pressure  $P_0$ . The osmotic pressure  $\pi$  of the liquid  $L$  with respect to  $L_0$  is then  $\pi = P - P_0$ .

When we allow  $\delta n$  quantities of the diffusing substance  $W$  to be transported from the liquid  $L_0$  towards the liquid  $L$ , then we find the equation for equilibrium:

$$\left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots \right)_P = (\zeta_0)_{P_0} \dots \dots \dots (2)$$

in which  $\zeta$  and  $\zeta_0$  represent the thermodynamical potentials of the unity of quantity of the liquids  $L$  and  $L_0$ . Consequently  $\zeta$  is a function of  $P x y \dots$  and  $\zeta_0$  a function of  $P_0$ .

When  $L$  is a binary liquid, which contains besides the diffusing substance  $W$  still only the substance  $X$ , then (2) passes into:

$$\left( \zeta - x \frac{\partial \zeta}{\partial x} \right)_P = (\zeta_0)_{P_0} \dots \dots \dots (3)$$

When we change  $x P$  and  $P_0$ , then follows:

$$-x r \cdot dx + \left( v - x \frac{\partial v}{\partial x} \right) dP = v_0 dP_0 \dots \dots \dots (4)$$

When we keep constant the external pressure  $P_0$  of the liquid  $L_0$ , then  $dP_0 = 0$  and  $dP = d\pi$ ; then it follows from (4):

$$d\pi = \frac{x r}{v - x \frac{\partial v}{\partial x}} dx \dots \dots \dots (5)$$



Hereby is defined the relation between the change  $dx$  of the concentration of the not-diffusing substance and the change  $d\pi$  of the osmotic pressure. In (5) is:

$$r = \frac{\partial^2 \xi}{\partial x^2} = \frac{RT}{x(1-x)} + \alpha \dots \dots \dots (6)$$

in which  $\alpha$  has a finite value. For very small values of  $x$ , as  $x \frac{\partial v}{\partial x}$  approaches then to zero, (5) passes into:

$$d\pi = \frac{RT}{v} \cdot dx \quad \text{or} \quad \pi = \frac{RT}{v} \cdot x \dots \dots \dots (7)$$

the well-known law of VAN 'T HOFF. When the concentration  $x$  of the not-diffusing substance becomes larger, then deviations of this law may occur; (5) remains valid, however.

When  $x$ , viz. the concentration of the not-diffusing substance  $X$  approaches to 1, then, as is apparent from (6) the numerator of (5) becomes very large. A small change of the concentration shall cause, therefore a very large change of the osmotic pressure.

We now distinguish two principal cases.

I. All liquids under consideration rest homogeneous; consequently no dimixtion into two liquids occurs.

As  $r$  is, therefore, always positive, the numerator of (5) is, therefore, also always positive.

In order to find the meaning of the denominator, we mix  $dn$  quantities  $W$  with one quantity  $L$ ; the total new volume  $v'$  becomes then:

$$v' = v + \left( v - x \frac{\partial v}{\partial x} \right) dn \dots \dots \dots (8)$$

In general shall be  $v' > v$ , unless with the mixing a contraction of volume occurs which is still larger than the volume of the added quantity of  $W$ . In general the denominator is positive, therefore; this is surely the case for small values of  $x$ , as  $v - x \frac{\partial v}{\partial x}$  only differs little then from  $v$ . As:

$$d \left( v - x \frac{\partial v}{\partial x} \right) = - x \frac{\partial^2 v}{\partial x^2} \cdot dx \dots \dots \dots (9)$$

it appears that the denominator may become negative only then, when the  $v, x$ -curve turns its convex side towards the concentration-axis. We now distinguish two cases.

$\alpha$ . The denominator of (5) is always positive.

From (5) follows: with increasing concentration of the not-diffusing substance, the osmotic pressure grows.

We draw in fig. 1 on the horizontal line  $WX$  the concentrations

and on the vertical axis the pressures  $P = P_0 + \pi$  of the osmotic equilibrium  $L + W$ . When we take  $W a_0 = P_0$ , then we get the osmotic pressure-curve  $a_0 b c d$ . Consequently in  $a_0$  the osmotic pressure is zero; in  $b, c$ , etc., it is represented by the length of the perpendiculars fallen on the line  $a_0 a'_0$ .

The direction of this curve in its beginning-point  $a_0$  is defined by (7)

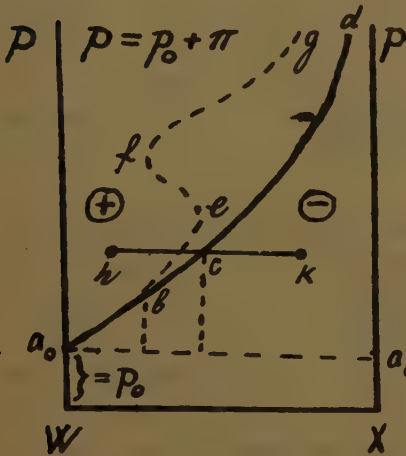


Fig. 1.

viz. the law of VAN 'T HOFF; in the vicinity of the line  $XP$ , it shows a straight ascension. The osmotic pressure-curve  $a_0 b c d$  divides the diagram into two fields, which we shall call the (+) field and the (—) field; the first one is indicated in the figure by an encircled +, the second one by an encircled —.

An arbitrary point  $h$  in the (+) field represents a liquid, which, under the pressure  $P_h$ , is not in osmotic equilibrium with the diffusing substance  $W$ , but contains too much

of this substance. When we keep the pressure constant, then it passes, depositing the substance  $W$  in the liquid  $c$ , which is in osmotic equilibrium under this pressure.

A point  $K$  in the (—) field represents a liquid, which contains too little of the substance  $W$ . Consequently it passes dissolving the diffusing substance  $W$  into the liquid  $c$  also.

We are able to deduce the osmotic pressure-curve also by other considerations.

We imagine viz. the diffusing substance  $W$  to be substituted by an imaginary state of this substance, which we shall call  $(W)$ . We define this imaginary state in such a way that the thermodynamical potential of  $(W)$  under all pressures is equal to  $(\zeta_0)_{P_0}$  viz. to that of the diffusing substance  $W$  under the pressure  $P_0$ .

When in (2)  $xy \dots$  approach to zero, then the first part becomes equal to the thermodynamical potential of the substance  $W$  under the pressure  $P$ ; when we call this  $(\zeta_W)_P$  then we have:

$$(\zeta_W)_P = (\zeta_0)_{P_0} + \int_{P_0}^P v dP \quad . \quad . \quad . \quad (10)$$

When we take  $P > P_0$  then is, therefore  $(\zeta_W)_P > (\zeta_0)_{P_0}$ ; when  $P < P_0$  then is  $(\zeta_W)_P < (\zeta_0)_{P_0}$ .

Instead of the osmotic equilibrium  $L + W$  we now take the equilibrium  $L + (W)$ ; as  $L$  represents herein the liquids, which are saturated with the imaginary substance  $(W)$  we shall call this the "saturation-equilibrium".

For this saturation-equilibrium we find the condition for equilibrium

$$\left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots \right)_P = (\zeta)_P \dots \dots \dots (11)$$

consequently the same as (2). Hence it follows, therefore:

we can replace an osmotic equilibrium  $L + W$  with the osmotic pressure  $\pi = P - P_0$  by the saturation-equilibrium  $L + (W)$  under the pressure  $P = P_0 + \pi$ .

When a liquid  $L$  has an osmotic pressure  $\pi = P - P_0$  then this liquid is in equilibrium under the pressure  $P = P_0 + \pi$  with the imaginary substance  $(W)$ ; and reversally.

The osmotic pressure-curve  $a, bcd$  of fig. 1 represents, therefore, also the liquids, which are saturated under the different pressures  $P$  with the substance  $(W)$ ; points in the  $(+)$  field represent super-saturated solutions, points in the  $(-)$  field unsaturated solutions.

Reversally we can also find this osmotic pressure-curve, when we deduce the saturation-curve of the substance  $(W)$  under variable pressure.

*b.* When we assume that the denominator of (5) may become also negative, then the osmotic pressure-curve may have a form as f.i.: the curve  $a, befg$  (fig. 1); on part  $fe$  then the osmotic pressure decreases at increasing concentration of the not-diffusing substance. Then there are liquids which have three different osmotic pressures.

When we consider, instead of the osmotic equilibrium  $L + W$  the saturation-equilibrium  $L + (W)$ , then along curve  $a, befg$  with increase of pressure the solubility of the substance  $(W)$  decreases firstly as far as  $e$ , further it increases as far as  $f$  and afterwards it decreases again.

II. Now we shall assume that there are also liquids  $L$ , which are dimixed into two other liquids.

When we wish to deduce the shape of the osmotic curve also now with the aid of (5) and other relations, then we have to take into consideration that  $r$  can also become negative.

However, we shall replace now the osmotic equilibrium  $L + W$  by the saturation-equilibrium  $L + (W)$ . Consequently we have only to seek for the saturation-curve of the substance  $(W)$  when liquids occur, which are dimixed.



Although those saturation-curves are known, yet we will for a moment indicate the way to deduce them graphically.

For this reason we draw on the horizontal axis (fig. 2) the concentrations and on the vertical axis the thermodynamical potentials

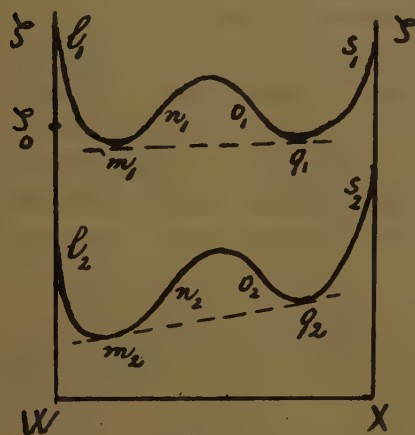


Fig. 2.

of the liquids. We represent  $(\xi_0)_{P_0}$  viz. the thermodynamical potential of the imaginary substance ( $W$ ) by point  $\xi_0$ . Under a pressure  $P_1 > P_0$  the  $\xi$ -curve has a form like  $l_1 m_1 n_1 o_1 q_1 s_1$ ; the point  $l_1$  is situated, as formerly is deduced from (10), above the point  $\xi_0$ . As we assume that dimixion may occur, in this  $\xi$ -curve two points of inflexion  $n_1$  and  $o_1$  occur. We can, therefore, also draw a double-tangent with the two points of contact  $m_1$  and  $q_1$ . Liquids, represented by points of  $l_1 m_1$  and  $q_1 s_1$  rest, therefore, homogeneous; the other liquids are dimixed in a complex of the two liquids  $m_1$  and  $q_1$ . The liquids, situated between  $m_1$  and  $n_1$  and those between  $o_1$  and  $q_1$  are metastable, the liquids between  $n_1$  and  $o_1$  are unstable ones.

We now imagine the tangents to be drawn in the points of inflexion  $n_1$  and  $o_1$ ; their points of intersection with the axis  $W\xi$  are called  $n'_1$  and  $o'_1$ . We now may distinguish several cases.

1. The point  $\xi_0$  is situated below the point of intersection  $n'_1$ . Only one tangent to the  $\xi$ -curve can be drawn from  $\xi_0$ ; consequently under the pressure  $P_1$  there is only one liquid, which is saturated with the substance ( $W$ ); consequently also: there is only one liquid with the osmotic pressure  $\pi = P_1 - P_0$ . This liquid is stable and is situated between  $q_1$  and  $s_1$ .

2. The point  $\xi_0$  is situated between  $n'_1$  and  $o'_1$ .

Now we can draw from  $\xi_0$  three tangents to the  $\xi$ -curve; consequently there are three liquids with the same osmotic pressure  $\pi = P_1 - P_0$ ; one of these liquids is stable, one metastable and one unstable. When the point  $\xi_0$  is situated above the double-tangent  $m_1 q_1$ , then the stable liquid is situated between  $l_1$  and  $m_1$ ; when  $\xi_0$  is situated below the double-tangent, then the stable liquid is situated between  $q_1$  and  $s_1$ .

When accidentally the point  $\xi_0$  is situated on the double-tangent then there are two stable liquids viz.  $m_1$  and  $q_1$ , which have the same osmotic pressure; the third one is unstable.

3. The point  $\xi_0$  is situated above the point  $o'_1$ .

As  $\zeta_0$  is situated below  $l_1$ ,  $\zeta_0$  is situated, therefore, between  $o'_1$  and  $l_1$ . Only one tangent can be drawn from  $\zeta_0$  now; consequently there is only one solution saturated with the substance ( $W$ ), consequently also only one liquid with the osmotic pressure  $\pi = P_1 - P_0$ . This liquid is stable and is situated between  $l_1$  and  $m_1$ .

On decrease of pressure all points of the  $\zeta$  curve shift downwards; its form changes therewith at the same time. Under a pressure  $P = P_0$  it goes through the point  $\zeta_0$ , which rests on its place at change of pressure; under a pressure  $P_2 < P_0$  it may be represented f.i. by curve  $l_2, m_2, n_2, o_2, q_2$ . As  $\pi = P_2 - P_0$  is negative now, the osmotic pressure is negative, therefore. We now may distinguish two cases.

4. The point  $\zeta_0$  is situated above the point of intersection  $o'_1$ .

Consequently no tangent can be drawn from  $\zeta_0$  to the  $\zeta$  curve; consequently there is also no liquid with the considered negative osmotic pressure.

5. The point  $\zeta_0$  is situated below the point of intersection  $o'_1$ .

Consequently from  $\zeta_0$  two tangents can be drawn to the  $\zeta$  curve; therefore there are under the pressure  $P_2$  two liquids, both saturated with the substance ( $W$ ), consequently also two liquids with the negative osmotic pressure  $\pi = P_2 - P_0$ . One of these liquids is metastable, the other one is unstable.

Firstly we imagine a very low pressure, so that the  $\zeta$  curve is situated far below the point  $\zeta_0$ ; on increase of  $P$  it then shifts upwards, under a pressure  $P = P_0$  it goes through the point  $\zeta_0$  and on further increase of pressure it comes above the point  $\zeta_0$ . As the  $\zeta$  curve changes also its form with this change of pressure, there may be also pressures, under which its concave part is disappearing, so that it gets downwardly totally a convex shape. When we consider at each stand of the  $\zeta$  curve the tangents from the point  $\zeta_0$  drawn to the  $\zeta$  curve, at which several of the cases mentioned sub 1—5 and their transition-forms may occur, then we find the following.

A. The saturation-curve of the substance ( $W$ ) and consequently also the osmotic pressure-curve consists of one single branch.

Then we may get a diagram as in fig. 3, in which the osmotic pressure-curve is represented by  $a, b, uvw, b, c$ ; the curves  $d, b, e_1$  and  $d, b, e_2$  are the limit-curves of the region of dimixtion. Starting from  $a_0$ , the osmotic curve comes in  $b_1$  under the pressure  $P_{b_1}$  in the region of dimixtion, it reaches in  $u$  a maximum- and afterwards in  $w$  a minimum-pressure and in  $b_2$  under a pressure  $P_{b_2} = P_{b_1}$  it leaves the region of dimixtion. The parts  $a, b_1$  and  $b_2, c$  represent

stable states, the parts  $b_1u$  and  $wb_2$  represent metastable states and part  $uvw$  unstable states. When the point  $w$  is situated below the line  $a_0a'_0$ , as is drawn in fig. 3, then there are also liquids (unstable and metastable) with negative osmotic pressure.

When we limit ourselves to stable states alone, then only one liquid belongs to each osmotic pressure  $\pi = P - P_0$ . However the two liquids  $b_1$  and  $b_2$  belong to the osmotic pressure  $\pi = P_{b_1} - P_0 = P_{b_2} - P_0$ ; those liquids are also in equilibrium with one another under the pressure  $P_{b_1} = P_{b_2}$ .

B. The saturation-curve of the substance ( $W$ ) and consequently also the osmotic pressure-curve consists of two parts, separated from one another.

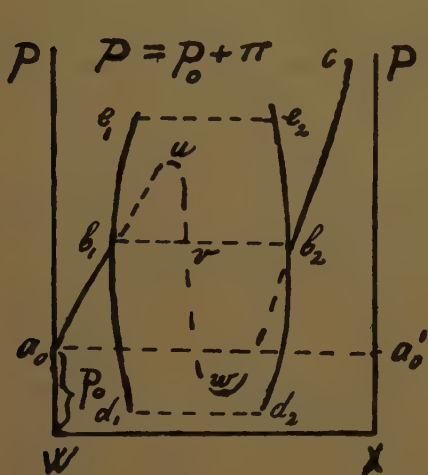


Fig. 3.

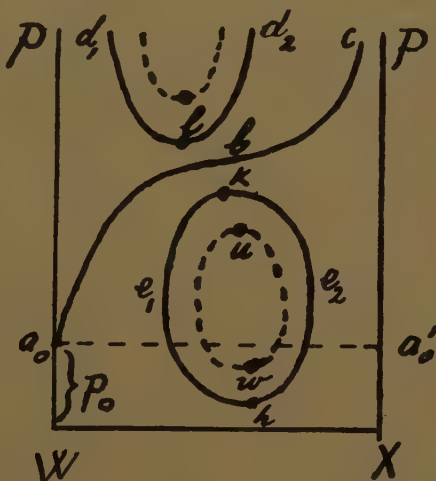


Fig. 4.

Then we may obtain a diagram as in fig. 4, in which the one part of the osmotic pressure-curve is represented by  $a_0bc$ , the other part by the closed curve  $uw$ . The latter is situated within the region of dimixtion with the limit-curves  $ke_1h$  and  $ke_2h$ , of which  $k$  and  $h$  represent the critical points. The part of curve  $uw$ , directed towards point  $e_1$ , represents unstable states, the part of this curve directed towards point  $e_2$ , represents metastable states.

The region of dimixtion can be situated also above the curve  $a_0bc$ ; this case is represented in fig. 4 by curve  $d_1ld_2$ . The dotted line within this region of dimixtion then represents the second branch of the osmotic pressure-curve.

When we limit ourselves to stable states, then to each definite osmotic pressure  $\pi = P - P_0$  belongs one liquid only.

In general the osmotic pressure-curve  $a_0bc$  shall ascend only



slowly in the vicinity of the critical point  $k$  (or  $l$ ) with increasing concentration of the not-diffusing substance  $X$ . In the point  $k$  (or  $l$ ) itself is viz.  $r = 0$ ; on curve  $a_0 b c$ , in the vicinity of this point  $k$  (or  $l$ )  $r$  is positive, but it may be still very small. When this is the case, then the above-mentioned follows at once from (5).

Between the figures 3 and 4 a transition-form exists. This occurs when the osmotic pressure-curve  $a_0 b c$  comes in contact with one of the regions of dimixtion f.i.  $kh$  in the critical point  $k$ . Then point  $u$  coincides with  $k$ . Curve  $a_0 b c$  then shows in  $k$  a point of inflexion with a horizontal tangent.

Till now we have assumed that the diffusing liquid  $W$ , with respect to which we define the osmotic pressure  $\pi = P - P_0$ , of a liquid  $L$ , has a constant external pressure  $P_0$ . Now we shall examine which influence has a change of  $P_0$  on the osmotic pressure  $\pi$ . We take a liquid of constant composition; consequently  $x$  in (3) is constant. From (3) now follows:

$$dP = \frac{v_0}{v - x \frac{\partial v}{\partial x}} dP_0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

As now  $d\pi = dP - dP_0$ , we find:

$$d\pi = - \frac{v_0 - v + x \frac{\partial v}{\partial x}}{v - x \frac{\partial v}{\partial x}} \cdot dP_0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When we bring the pressure of the diffusing liquid  $W$  from  $P_0$  to  $P_0 + dP_0$ , then the change  $dP$  of the pressure and the change  $d\pi$  of the osmotic pressure of the liquid  $L$  are defined by (12) and (13). Consequently in figs. 1, 3 and 4 the straight line  $a_0 a'_0$  shifts upwards a part  $dP_0$ , each point of the osmotic pressure-curve a part  $dP$  (defined by 12). As, however,  $dP$  depends also on  $x$ , all points of the osmotic pressure-curve don't shift upwards in the same extent; consequently also this curve changes its form, so that the osmotic pressure changes also. This follows at once also from (13) from which it appears at the same time that the change  $d\pi$  of the osmotic pressure depends also on the composition of the liquid.

In the figs. 3 and 4 on change of the pressure  $P_0$  the osmotic curves shift, therefore, while the regions of dimixtion rest on their places of course. In fig. 3 the points  $b_1$  and  $b_2$  shift, therefore, along the curves  $d_1 e_1$  and  $d_2 e_2$ ; in fig. 4 the osmotic pressure-curve either approaches more or moves further from the critical point  $k$  or  $l$ .

On further change of  $P_0$  the osmotic curve may go now through the point  $l$ ; on still more change fig. 4 passes then into fig. 3.

Consequently we find: the osmotic pressure of a liquid  $L$  with respect to the diffusing substance  $W$  depends on:

1. the concentration of the liquid  $L$ .
2. the external pressure  $P_0$  of the diffusing liquid  $W$ . It may depend also on this pressure  $P_0$ , whether the osmotic pressure-curve consists of one branch (fig. 3) or of more branches (fig. 4).

As the coefficient of  $dP_0$  in (13) may be as well positive as negative, the osmotic pressure may either grow or diminish. However the osmotic pressure shall grow at increase of  $P_0$  with liquids which contain only little of the not-diffusing substance  $X$ .

From (13) and also from (7) it follows viz.:

$$\frac{d\pi}{dP_0} = -\frac{1}{v} \frac{\partial v}{\partial P_0} \cdot \pi = -\frac{RT}{v^2} \frac{\partial v}{\partial P_0} \cdot \pi \quad . \quad . \quad . \quad (14)$$

in which  $\frac{\partial v}{\partial P_0}$  is negative of course. As  $\frac{\partial v}{\partial P_0}$  is only very small, the change of the osmotic pressure is also very small. With small changes of  $P_0$  the osmotic pressure practically does not change.

VAN 'T HOFF has compared the osmotic pressure of a liquid  $L$  with the pressure which the not-diffusing substance  $X$  should exert, when in gas-state this should occupy the volume  $v$  of the liquid  $L$ .

Following this comparison in large lines we might say that in fig. 1 the substance  $X$  behaves like a gas, far above its critical temperature  $T_k$ , in fig. 4 as a gas, in the vicinity of this temperature and in fig. 3 as below  $T_k$ . On branch  $a, b_1$  the substance  $X$  should be then in gaseous state, on branch  $b, c$  in liquid state. Further we should have to assume that this critical temperature, and, therefore, also the behaviour of the substance  $X$  depends on the pressure  $P_0$  of the diffusing substance.

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*(To be continued).*

**Chemistry.** — “*Equilibria in systems in which phases, separated by a semipermeable membrane.*” II. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 25, 1924).

### *Isotonic liquids.*

We take two liquids  $L_1$  and  $L_2$  which are separated from one another at a definite temperature  $T$  and pressure  $P$  by a semipermeable membrane, which permits to diffuse one or more of the substances.

We shall say now that both liquids are isotonic with respect to those diffusing substances, at that  $T$  and  $P$ , at which they are in osmotic equilibrium with one another. The total thermodynamical potential is not allowed to change, therefore, when small quantities of the diffusing substances pass from the one liquid towards the other.

We give to  $L_1$  and  $L_2$  the composition:

$$a_1 \text{ Mol } A + b_1 \text{ Mol } B \dots + x_1 \text{ Mol } X + y_1 \text{ Mol } Y + \dots w_1 \text{ Mol } W$$

$$m_2 \text{ Mol } M + n_2 \text{ Mol } N \dots + x_2 \text{ Mol } X + y_2 \text{ Mol } Y + \dots w_2 \text{ Mol } W$$

in which

$$w_1 = 1 - a_1 - b_1 \dots - x_1 - y_1 \dots$$

$$w_2 = 1 - m_2 - n_2 \dots - x_2 - y_2 \dots$$

Consequently we have the general case that both liquids contain, besides the common substances  $X Y \dots W$ , also not-common substances;  $A B \dots$  appear viz. in  $L_1$  only,  $M N \dots$  in  $L_2$  only.

When there is only one diffusing substance f.i.  $W$  then the equation of equilibrium is:

$$\varphi_1 = \varphi_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which

$$\varphi_1 = \zeta_1 - a_1 \frac{\partial \zeta_1}{\partial a_1} - b_1 \frac{\partial \zeta_1}{\partial b_1} \dots - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots$$

$$\varphi_2 = \zeta_2 - m_2 \frac{\partial \zeta_2}{\partial m_2} - n_2 \frac{\partial \zeta_2}{\partial n_2} \dots - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots$$

Consequently (1) is a function of  $TP$  and all variables of both the liquids.



Is  $X$  the diffusing substance, then we find:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial x_1} = \varphi_2 + \frac{\partial \zeta_2}{\partial x_2} \quad . . . . . (2)$$

Is  $Y$  the diffusing substance, then is true:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial y_1} = \varphi_2 + \frac{\partial \zeta_2}{\partial y_2} \quad . . . . . (3)$$

etc. When all common substances  $WXY\dots$  can diffuse, then the equations (1)(2)(3) . . . are valid at the same time.

We now shall deduce some properties, and imagine  $T$  and  $P$  to be constant.

When we assume that the liquid  $L_1$  is saturated with the solid substance  $W$ , then is valid for this equilibrium  $L_1 + W$  the equation:

$$\varphi_1 = \zeta_W \quad . . . . . (4)$$

in which the  $\zeta$  of the solid substance  $W$  is indicated by  $\zeta_W$ . When the liquid  $L_2$  is also saturated with  $W$ , then is true for this the relation  $\varphi_2 = \zeta_W$ . As from both those equations the relation (1) follows, both liquids are, therefore, isotonic with respect to the substance  $W$ .

When both liquids are saturated with the solid substance  $X$ , then are valid the two equations:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial x_1} = \zeta_X \quad \text{and} \quad \varphi_2 + \frac{\partial \zeta_2}{\partial x_2} = \zeta_X \quad . . . . . (5)$$

in which  $\zeta_X$  represents the  $\zeta$  of the solid substance  $X$ . From both those equations (2) follows, so that the two liquids are isotonic with respect to the substance  $X$ . Consequently we find:

two liquids, both saturated with a same solid substance, are isotonic with respect to this substance.

All liquids, in equilibrium with ice, are, therefore, isotonic with respect to water, whatever substances are occurring in each of those liquids.

All liquids, saturated with sugar or urea etc. or with sugar + urea etc. are, therefore, isotonic with respect to sugar or urea etc. or to sugar + urea etc., whatever substances each of those substances still contains.

In the same way we can deduce also:

when a liquid is saturated with  $X + Y + Z$  and another liquid with  $X + Y + U$ , then they are isotonic with respect to  $X$  and  $Y$ , but not with respect to  $U$  and  $Z$ ;

when a liquid  $L$  is in equilibrium with a solid substance  $W$ , then all liquids which are isotonic with  $L$  with respect to this substance  $W$ , may be in equilibrium also with the solid substance  $W$ ; when two liquids  $L_1$  and  $L_2$  are isotonic with respect to  $XY$  and  $Z$  and  $L_1$  and  $L_2$  are isotonic with respect to  $XY$  and  $U$ , then  $L_1$  and  $L_2$  are isotonic with respect to  $X$  and  $Y$ .

We now assume that the liquids  $L_1$  and  $L_2$  are both in equilibrium with a vapour, which contains only one substance f.i.  $W$ . We then have the equations for equilibrium:

$$\varphi_1 = \zeta_W \quad \text{and} \quad \varphi_2 = \zeta_W \dots \dots \dots (6)$$

in which  $\zeta_W$  represents the  $\zeta$  of the substance  $W$  in vapour-form. As from both those equations the relation (1) follows again, both liquids are isotonic, therefore, with respect to the substance  $W$ . Consequently follows from this:

two liquids, both in equilibrium with a single vapour, are isotonic with respect to the substance of which this vapour consists.

All liquids in equilibrium with water-vapour are, therefore, isotonic with respect to water, whatever substances each of those liquids still contains.

Of course the same is true for liquids, in equilibrium with alcohol-vapour or benzene-vapour etc.

We find also:

when a liquid  $L$  is in equilibrium with a vapour  $W$ , then all liquids which are isotonic with  $L$  and contain no other volatile substances than  $W$ , may also be in equilibrium with the vapour  $W$ .

We don't consider it necessary to draw once more the attention to the fact that the deductions mentioned above are only valid for constant  $T$  and  $P$ .

We now take in a system of  $n$  components at a definite  $T$  and  $P$  a liquid  $L_1$  with the definite composition:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y + z_1 \text{ Mol } Z \dots + (1 - x_1 - y_1 - z_1 \dots) \text{ Mol } W.$$

We now put the question: which other liquids  $L$  are isotonic with  $L_1$  at the same  $T$  and  $P$  when  $W$  is the diffusing substance.

When we represent the composition of  $L$  by:

$$x \text{ Mol } X + y \text{ Mol } Y + z \text{ Mol } Z \dots + (1 - x - y - z) \text{ Mol } W$$

then must, therefore, be satisfied:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} - z_1 \frac{\partial \zeta_1}{\partial z_1} \dots \quad (7)$$

As  $x_1 y_1 z_1 \dots$  have a definite value, the second part of (7) has, therefore, a definite value also; when we represent this by  $\xi_{(W)}$  then  $xyz \dots$  must satisfy:

$$\xi - x \frac{\partial \xi}{\partial x} - y \frac{\partial \xi}{\partial y} - z \frac{\partial \xi}{\partial z} \dots = \xi_{(W)} \dots \dots \dots (8)$$

Consequently at constant  $T$  and  $P$  in a system of  $n$  components an infinite number of liquids exists, which are mutually isotonic with respect to a definite substance. We shall refer later to the special case that  $n = 2$ .

We may still give to (8) a meaning, by which the mutually isotonic liquids may be brought into combination with other equilibria.

We imagine for this the diffusing substance  $W$  in an imaginary solid state which we shall call  $(W)$ . We define this imaginary state in such a way that the thermodynamical potential of this substance  $(W)$  is equal to  $\xi_{(W)}$ .

When we consider the equilibrium  $L + (W)$ , we see that equation (8) is also valid for this. Hence follows:

all liquids which are isotonic with respect to the substance  $W$ , are saturated with the imaginary solid substance  $(W)$ ;

and reversally: all liquids which are saturated with the imaginary solid substance  $(W)$  are isotonic with respect to the substance  $W$ .

By giving other values to  $x_1 y_1 z_1 \dots$  in (7) we can change the value of  $\xi_{(W)}$  in (8). It is evident that  $\xi_{(W)}$  may get an infinite number of values so that we must distinguish also an infinite number of modifications of the imaginary substance  $(W)$  which pass into one another without interruption. Let us consider some of those modifications, which we shall represent by  $(W_1)$ ,  $(W_2)$ ,  $(W_3)$  etc. with thermodynamical potentials  $\xi_{(W_1)}$ ,  $\xi_{(W_2)}$ ,  $\xi_{(W_3)}$  etc.

We now take the equations:

$$\varphi = \xi_{(W_1)} \quad \varphi = \xi_{(W_2)} \quad \varphi = \xi_{(W_3)} \quad \dots \dots \dots (9)$$

in which  $\varphi$  represents the first part of equation (8). The first one of those equations represents all liquids which are mutually isotonic with respect to the substance  $W$ , or the liquids which are saturated with the modification  $(W_1)$ . We shall say that all those liquids belong to the „isotonic group  $(W_1)$ “. The second equation also represents a group of liquids which are mutually isotonic with respect to the substance  $W$ ; however they are saturated with the modification  $(W_2)$ . Those liquids form the „isotonic group  $(W_2)$ “. The third equation represents the liquids of the isotonic group  $(W_3)$  etc.



Consequently all liquids of the isotonic group ( $W_1$ ) are mutually isotonic; also all liquids of the isotonic group ( $W_2$ ); etc. Liquids of two different isotonic groups, however, are not isotonic with one another.

We find, therefore:

in a system of  $n$  components at constant  $T$  and  $P$  exists an infinite number of isotonic groups, each of which consists of an infinite number of liquids. All liquids of a same isotonic group are mutually isotonic, but liquids of different isotonic groups are not isotonic with one another.

In order to show the latter we take two liquids  $L_1$  and  $L_2$  of the composition:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y + \dots (1-x_1-y_1 \dots) \text{ Mol } W$$

and

$$x_2 \text{ Mol } X + y_2 \text{ Mol } Y + \dots (1-x_2-y_2 \dots) \text{ Mol } W.$$

We assume that  $L_1$  belongs to the isotonic group ( $W_1$ ) and  $L_2$  to the isotonic group ( $W_2$ ). We then have the two relations:

$$\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots = \zeta_{(W_1)} \quad \dots \quad (10)$$

$$\zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots = \zeta_{(W_2)} \quad \dots \quad (11)$$

When we take  $n_1$  quantities  $L_1$  and  $n_2$  quantities  $L_2$  then is the total thermodynamical potential

$$Z = n_1 \zeta_1 + n_2 \zeta_2.$$

When  $\Delta n_1$  quantities of the substance  $W$  diffuse from  $L_1$  to  $L_2$  then we find:

$$\Delta Z = \left( -\zeta_1 + x_1 \frac{\partial \zeta_1}{\partial x_1} + y_1 \frac{\partial \zeta_1}{\partial y_1} \dots + \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \right) \Delta n$$

or

$$\Delta Z = [\zeta_{(W_2)} - \zeta_{(W_1)}] \Delta n \quad \dots \quad (12)$$

As the second part of (12) is not zero, the two liquids are not in osmotic equilibrium, therefore, but the substance  $W$  diffuses.

The direction of the diffusion must now be in such a way that  $\Delta Z$  is negative. When we take  $\zeta_{(W_1)} > \zeta_{(W_2)}$  then  $\Delta n$  must be positive, therefore; consequently the substance  $W$  diffuses from  $L_1$  to  $L_2$ . Consequently we may say:

the substance  $W$  diffuses from the liquid in which  $\zeta_{(W)}$  has the largest value, to a liquid with smaller value of  $\zeta_{(W)}$ .

As in the case above-discussed the substance  $W$  diffuses from  $L_1$  to  $L_2$ , we shall say that the „membrane-diffusion-pressure” or shortly the “diffusion-pressure” of the substance  $W$  is larger in  $L_1$  than in  $L_2$ . Consequently we may say also: the greater  $\zeta_{(W)}$  is in a liquid, the greater the diffusion-pressure of substance  $W$  in that liquid is.

We shall refer later to some other general properties of isotonic groups.

*Isotonic liquids in binary systems.*

Above we have seen already that the general considerations are not valid in every respect for binary systems. When we take viz. a binary system with the components  $X$  and  $W$  then (8) passes into:

$$\zeta - x \frac{\partial \zeta}{\partial x} = \zeta_{(W)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which defines at constant  $T$ ,  $P$  and  $\zeta_{(W)}$  an isotonic group of liquids. But as in (13)  $x$  is no more variable, we can only satisfy (13) by one or by some definite values of  $x$ . Consequently the isotonic group consists also of only one or of some definite liquids and not, as in the general case, of an infinite number.

We imagine to be drawn on an horizontal axis the composition and on a vertical axis the  $\zeta$ 's of the binary liquids. When in the binary system dimixtion occurs, then the  $\zeta$  curve has a form like curve  $l_1s_1$  in fig. 2 of the previous communication; when all liquids rest homogeneous, then it is convex downward in each point. We now take on the axis  $W\zeta$  (fig. 2 l.c.) a part  $W\zeta_0 = \zeta_{(W)}$ . The points of contact of the tangents drawn from the point  $\zeta_0$  indicate then isotonic liquids, consequently liquids of a same isotonic group ( $W$ ).

When the  $\zeta$  curve is convex downward then only one tangent to the curve can be drawn at each position of  $\zeta_0$ ; each isotonic group consists, therefore, of one liquid only; consequently at constant  $T$  and  $P$  there are no isotonic liquids.

When the  $\zeta$  curve has a form like curve  $l_1s_1$  in fig. 2 (l.c.) then at definite situations of the point  $\zeta_0$  three tangents may be drawn. The corresponding isotonic groups then consist each of 3 liquids, of which, however, only one is stable. However, there is one isotonic group, which contains two stable (and one unstable) liquids viz. when the point  $\zeta_0$  coincides with the point of intersection of the axis  $W\zeta$  and the double-tangent  $m_1q_1$ . Limiting ourselves to stable states only, then follows, therefore:

in a binary equilibrium in which dimixtion may occur, at given  $T$  and  $P$  only two isotonic liquids exist. They are viz. the two

liquids which can be in equilibrium with one another at that  $T$  and  $P$ ; consequently they are isotonic with respect to both the components.

We shall refer to some properties when discussing the ternary systems.

### *Isotonic liquids in ternary systems.*

#### *Isotonic curves.*

For ternary liquids with the components  $X$   $Y$  and  $W$  (8) passes into:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = \zeta_{(W)} \quad . \quad . \quad . \quad (14)$$

which defines at constant  $T$ ,  $P$  and  $\zeta_{(W)}$  the liquids of an isotonic group ( $W$ ). As (14) represents a curve, it follows, therefore:

the liquids of an isotonic group ( $W$ ) are represented in a concentration diagram by a curve; we call this the „isotonic  $W$ -curve”.

As  $\zeta_{(W)}$  may have an infinite number of values, consequently there exists at constant  $T$  and  $P$  an infinite number of those curves; they are differing by the diffusion-pressure of the substance  $W$ , which grows with the increase of  $\zeta_W$ .

In fig. 1, in which  $X$   $Y$  and  $W$  represent the three components, some isotonic  $W$ -curves are drawn a.o. the curves  $ad$ ,  $eh$  and  $im$ . Consequently all liquids of curve  $ad$  are mutually isotonic with respect to the substance  $W$ ; the same is true for all liquids of  $eh$ ,

$im$  etc. Liquids of different curves are not isotonic, however, f.i. liquid  $b$  not with  $e$  or  $g$  or  $l$  etc.

We may deduce the isotonic  $W$ -curves also in the following way. We imagine in fig. 1 the  $\zeta$ 's of all liquids at constant  $T$  and  $P$  to be drawn perpendicular to the plane of design. We then get a  $\zeta$ ' surface  $W'X'Y'$ ; the lines  $WW'$ ,  $XX'$  and  $YY'$  represent then the  $\zeta$ 's of the substances

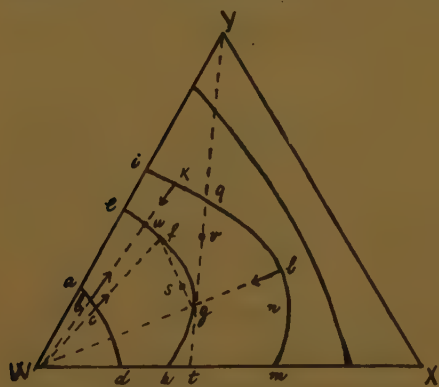


Fig. 1.

$W$   $X$   $Y$  in liquid state. We now take on the axis  $WW'$  a point  $w$  in such a condition that  $Ww = \zeta_{(W)}$ ; we draw a cone which has its top in  $w$  and which touches the  $\zeta$ -surface. The projection of the tangent-curve on the plane  $XYW$  is then the isotonic  $W$ -curve, belonging to this definite  $\zeta_{(W)}$ . When we change  $\zeta_{(W)}$  then we get also another isotonic curve.



Following this way we can deduce easily different properties; firstly we shall assume herewith, that no dimixtion into two or more liquids can occur, so that the  $\zeta$  surface is in each point convex downward. We find a.o.:

1. Each isotonic  $W$ -curve has two terminating-points; the one is situated on the line  $WX$ , the other on  $WY$  of the triangle (fig. 1).

2. Each straight line, drawn through the point  $W$ , intersects the isotonic  $W$ -curve in one point only.

3. Two different isotonic curves can never touch or intersect one another.

4. The isotonic  $W$ -curves are situated the nearer to the point  $W$ , the greater  $\zeta_{(W)}$  is. When  $\zeta_{(W)}$  becomes  $= \zeta_W$  (viz. the thermodynamical potential of the liquid  $W$ ) then this curve shrinks to the point  $W$  itself.

5 The diffusion-pressure of the substance  $W$  is equal in all liquids of an isotonic  $W$ -curve; however, it is greater, the nearer this curve is situated to the point  $W$ .

It is only too clear that all this is also true for the substances  $X$  and  $Y$ .

In order to find the form of the curves in the vicinity of the point  $W$ , we put:

$$\zeta = \varphi + RT(x \log x + y \log y).$$

(14) then passes into:

$$\varphi - x \frac{\partial \varphi}{\partial x} - y \frac{\partial \varphi}{\partial y} - RT(x + y) = \zeta_{(W)} \quad . \quad . \quad . \quad (15)$$

when we represent the value of  $\varphi$  for  $x = 0$  and  $y = 0$  by  $\varphi_0$ , then (15) passes into:

$$RT(x + y) = \varphi_0 - \zeta_{(W)} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which data of second and higher order are neglected and the second part has a small positive value. The isotonic  $W$ -curve is, therefore, in the vicinity of the point  $W$  a small straight line, which intercepts equal parts from the two axes. On further distance of the point  $W$  those curves are curled generally. In the vicinity of the point  $W$  the liquids, in which the diffusion-pressure of the substance  $W$  is the same, have also the same concentration of this substance  $W$ ; at a greater distance this is no more the case.

We now take two liquids  $b$  and  $k$  (fig. 1) which are situated on a straight line, going through point  $W$  and we separate those liquids by a semi-permeable membrane, which allows to pass the substance  $W$  only. As the diffusion-pressure of the substance  $W$  is larger in the liquid  $b$  than in  $k$ , consequently  $W$  shall diffuse from  $b$  to  $k$ ;

the two liquids move, therefore, towards one another in the direction of the little arrows. The diffusion-pressure of the substance  $W$  decreases, therefore, continually in the moving liquid  $b$ , in  $k$ , however, it increases. Consequently the diffusion will continue till both liquids reach the same isotonic  $W$ -curve; therefore, till they get the same composition. When  $u$  is the complex of the two liquids  $b$  and  $k$  then the result of the membrane-diffusion is, therefore, that both the liquids get the composition  $u$ . Of course the same is true also for binary liquids  $WX$  and  $WY$ .

Quite another case it is, however, when both the liquids are not situated on a straight line, going through  $W$ ; let us take f.i. the liquids  $c$  and  $l$ , the complex of which we shall represent by point  $s$ . At the membrane-diffusion of  $W$  therefore  $c$  shifts in the direction of the little arrow away from point  $W$  and  $l$  shifts in the direction of the little arrow towards point  $W$ ; of course the complex remains represented by point  $s$ . This membrane diffusion will continue till the one liquid is arrived in  $f$  and the other one in  $g$ ; the points  $f$ ,  $s$  and  $g$  are situated on a straight line and  $f$  and  $g$  on the same isotonic  $W$ -curve; the diffusion-pressure is then equal in both liquids. Consequently the result of the membrane diffusion is the birth of the liquids  $f$  and  $g$ .

The line  $fsg$  is drawn in fig. 1 approximately parallel to the line  $XY$ ; the liquids  $f$  and  $g$  have, therefore, approximately the same concentration of the substance  $W$ ; however, this line can be situated also in such a way that the concentration of  $W$  in the liquid  $f$  is larger than in  $g$  and reversally.

Now we will say of two substances the one of which has a larger concentration of the substance  $W$  than the other one, that the one is  $W$ -concentrated and the other one  $W$ -poor. We may say now:

at membrane-diffusion of the substance  $W$  between two liquids the  $W$ -concentrated may rest in this state, but it may become also  $W$ -poor.

Let us take in fig. 1 the liquids  $K$  and  $n$ , of which  $K$  is the  $W$ -concentrated and  $n$  the  $W$ -poor liquid. Imagining the isotonic  $W$ -curve drawn through  $n$ , then it appears that the diffusion-pressure of the substance  $W$  is larger in liquid  $n$  than in  $K$ ; consequently the substance  $W$  shall diffuse from  $n$  to  $K$ . We find, therefore:

at membrane-diffusion a substance  $W$  can go from a  $W$ -poor liquid to a  $W$ -concentrated liquid.

It follows from those considerations that the diffusion-pressure of a substance  $W$  in a liquid is not only dependent on the concentration of this substance  $W$ , but also on other substances, which are present in this liquid.

Let us take now the binary liquid  $d$  and let us add to this the new substance  $Y$ . Going from point  $d$  towards  $Y$  we now intersect isotonic  $W$  curves of steadily diminishing diffusion-pressure; consequently addition of  $Y$  causes decrease of the diffusion-pressure of the substance  $W$ .

However, when we add the new substance  $Y$  to the liquid  $t$ , then the phenomena become different; we assume viz. that the line  $tY$  touches the curve  $eh$  in  $g$ . We imagine in fig. 1 to be drawn through point  $t$  the isotonic  $W$ -curve, which intersects the line  $tY$  in  $v$ . Consequently the diffusion-pressure increases starting from  $t$ , reaches a maximum in  $g$  and decreases at further addition of  $Y$ ; then in  $v$  the diffusion-pressure is again the same as in  $t$ ; in  $q$  it is lower.

We find, therefore:

the diffusion-pressure of a substance in a binary mixture can as well decrease as increase by addition of a new substance; in the latter case this pressure goes through a maximum, so that at last it decreases again.

We take the liquids  $L_1$  and  $L_2$  with the composition:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y \dots + (1-x_1-y_1 \dots) \text{ Mol } W$$

and

$$x_2 \text{ Mol } X + y_2 \text{ Mol } Y \dots + (1-x_2-y_2 \dots) \text{ Mol } W,$$

and we keep the pressure  $P$  constant. When the pure liquid  $W$  under a pressure  $P_1$  is in osmotic equilibrium with the liquid  $L_1$ , then is the osmotic pressure  $\pi_1 = P - P_1$  of  $L_1$  defined by:

$$\left( \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots \right)_P = (\zeta_0)_{P_1} \dots \dots (17)$$

in which the second part represents the  $\zeta$  of the pure liquid  $W$  under the pressure  $P_1$ . The osmotic pressure  $\pi_2 = P - P_2$  of the liquid  $L_2$  with respect to the pure liquid  $W$  under a pressure  $P_2$  is defined by:

$$\left( \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \right)_P = (\zeta_0)_{P_2} \dots \dots (18)$$

when we represent the first part of (17) by  $\zeta_{(W_1)}$  and that of (18) by  $\zeta_{(W_2)}$  then follows:

$$(\zeta_{(W_1)} - \zeta_{(W_2)}) = (\zeta_0)_{P_1} - (\zeta_0)_{P_2} = \int_{P-\pi_2}^{P-\pi_1} v_0 dP \dots \dots (19)$$



in which  $v_0$  is the volume of the pure liquid. When this volume changes only little with the pressure, then with approximation (19) passes into:

$$\zeta_{(W_1)} - \zeta_{(W_2)} = (\pi_2 - \pi_1) v_0 \dots \dots \dots (20)$$

According to the sign of the first part of (19) or (20) being positive or negative, the membrane-diffusion-pressure of the substance  $W$  in the liquid  $L_1$  is larger or smaller than in  $L_2$ .

Consequently we may say:

the membrane-diffusion-pressure of a substance  $W$  in a liquid  $L$  under a pressure  $P$  is the larger (smaller), the smaller (larger), the osmotic pressure of this liquid  $L$  with respect to the pure liquid  $W$  is.

When the substance  $W$  diffuses by a membrane from the liquid  $L_1$  to  $L_2$ , we have said that the diffusion-pressure of the substance  $W$  in liquid  $L_1$  is larger than in  $L_2$ . However, we might say also that the "osmotic  $W$ -attraction" of liquid  $L_1$  is smaller than that of  $L_2$ . Then in the previous deductions we have to substitute everywhere larger (smaller) diffusion-pressure by smaller (larger) "osmotic attraction". Therefore the property mentioned sub 5 f.i. will become:

the osmotic  $W$ -attraction is the same for all liquids of an isotonic  $W$ -curve; however, the nearer this curve approaches point  $W$  the smaller the osmotic  $W$ -attraction is.

*Leiden.*

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*(To be continued).*

**Chemistry.** — “*On relatively asymmetrical synthesis in the case of Complex Salts of heavy Metals.*” By Dr. J. LIFSCHITZ. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of September 27, 1924).

On boiling an aqueous solution of rac. Alanine with cobalt-hydroxyde LEY and WINKLER <sup>1)</sup> obtained two complex cobaltic salts of alanine, the first of which, the red coloured  $\beta$ -form, appeared to be nearly insoluble in water, whilst the second or  $\alpha$ -form, having a violet red colour, was moderately soluble in water even of 25°. According to LEY and WINKLER these complex salts are stereoisomerides, differing only in the arrangement of the three coordinated molecules of alanine. No other products of reaction were obtained, the yield of the reaction-product being a fairly good one. In a later paper LEY <sup>2)</sup> however mentions another hydrate of the violet cobaltic salt of alanine, which was obtained incidentally. The existence of such hydrates is, of course, without any direct importance for the views advanced by this author.

The properties of both complex salts are, in so far as they were investigated, in perfect harmony with LEY's views, and, up to this date, no objections have been brought forward against the stereoisomerism of these cobaltic salts. Moreover A. WERNER <sup>3)</sup> has shown, that an isomerism of a perfectly analogous character is observed in the case of the *flavo-dinitro-ethylenediamine-propylenediamine-cobaltic salts*.

In connection with my investigations <sup>4)</sup> on rotatory dispersion of coloured active compounds, it seemed interesting to compare firstly active triacido-triammine-cobalti-complexes with the hexammine and hexacido salts, and secondly to study the stereoisomerides of the *Trialanine-cobaltic-type*. As the main difference of these latter only consists in a relatively small variation of the symmetry of the molecule as a whole, it might be expected, that some conclusions about the influence of molecular symmetry on the rotation of such complexes could be drawn. Pure d-Alanine was prepared in relatively

<sup>1)</sup> Ber. **42**, 3894 (1909).

<sup>2)</sup> Ber. **45**, 372 (1912).

<sup>3)</sup> Helv. **1**, 5 (1918).

<sup>4)</sup> Zeitschr. f. wissenschaft. Photogr. **19**, 212 (1920).

Zeitschr. f. physikal. Chem. **105**, 27 (1923).

large amounts from silk-waste, following E. FISCHER's method <sup>1)</sup>. The obtained dextrogyrate product was carefully fractionated and a fraction, showing the same rotation as indicated by this author for pure d-Alanine, was boiled with cobaltic-hydroxyde according to the method of LÉY. The hydroxyde was precipitated from pure aqueous

*Specific Rotation  
in Grades.*

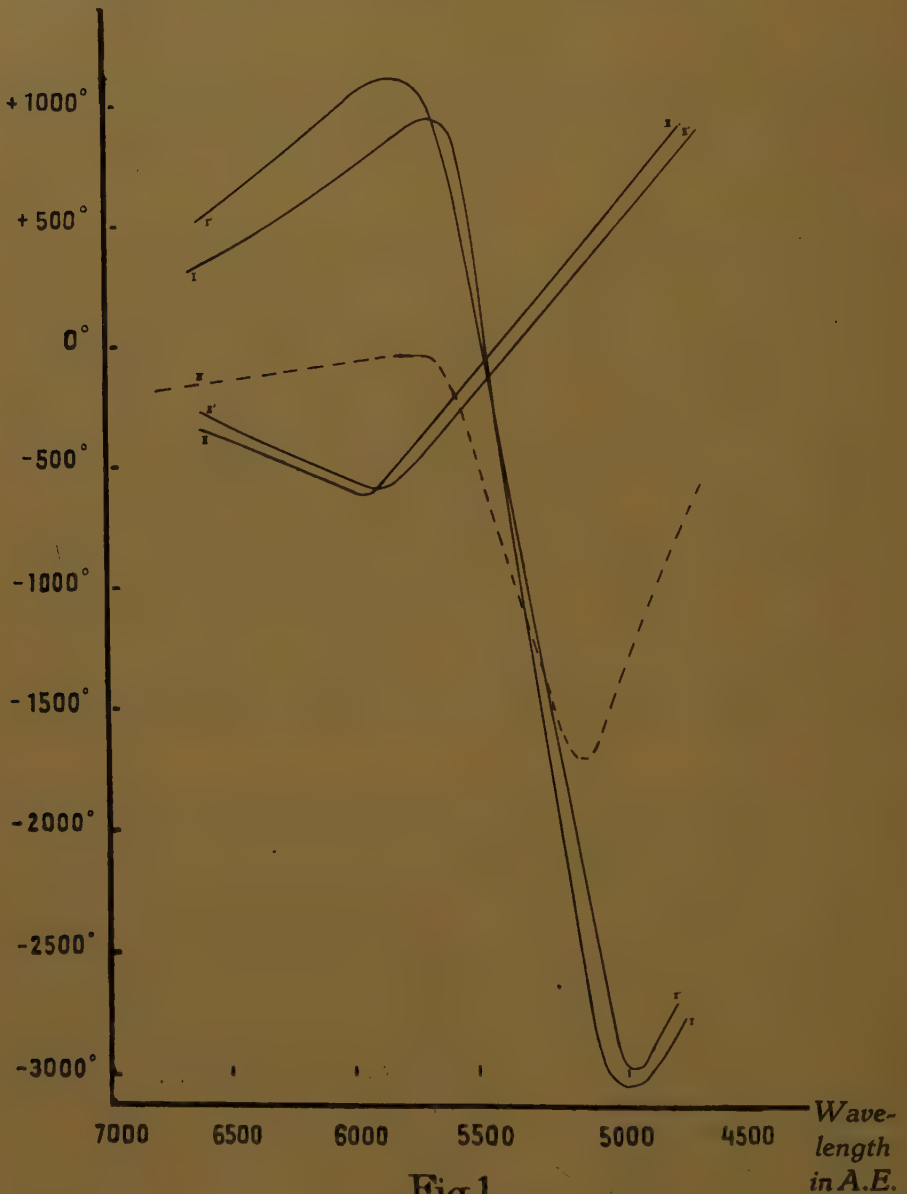


Fig.1

<sup>1)</sup> Ber. 39, 462.



cobaltchloride or -sulphate by an alkali-solution of bromine, the precipitate was filtered and thoroughly washed with hot water.

The red coloured isomeride of the *tri-d-alanine-cobaltic* salt obtained is perfectly insoluble in water. It is freed from cobaltic-oxyde and obtained in a pure state by repeatedly suspending it in aqueous solutions of sulphurous acid. A fairly good quantity was obtained by repeating this procedure. The substance readily dissolves, like the inactive compound, in 50 %  $\text{H}_2\text{SO}_4$  aq. without any change; the rotation of this solution is shown by the curve III of fig. 1.

The mother-liquors from the (crude) red *tri-d-alanine-cobaltic* salt are deep violet in colour. On fractional crystallization, first a violet salt was obtained, which in all points corresponded to the violet inactive isomeride of LEY. It was carefully recrystallized from boiling water, and beautiful small needles were obtained, containing 1 molecule of water. The rotations of this  $\alpha$ -salt in aqueous and 50 %  $\text{H}_2\text{SO}_4$  aq. solutions, are shown by the curves I and I' of fig. 1.

The mother-liquors of the  $\alpha$ -salt contain, besides further quantities of this, a second, extremely soluble and more purple coloured salt,  $\alpha'$ , which can be isolated with some difficulty. It is firstly freed from greater quantities of the  $\alpha$ -salt by fractional crystallization, and finally freed from the last traces of this and of d-Alanine, by repeated precipitation from a fairly concentrated solution by 97 % alcohol. A great deal of  $\alpha'$ -compound remains in the aqueous-alcoholic liquid, from which it is isolated by evaporation; it was washed with 97 % alcohol, and purified, until no alteration of the rotation is any more observed. The rotation of the somewhat hygroscopic salt is shown by the curves II and II' in water and 50 %  $\text{H}_2\text{SO}_4$  aq. respectively.

In order to establish the constitution of the  $\alpha'$ -salt, both the  $\alpha$ - and the  $\alpha'$ -complexes were analysed, and the following data obtained:

Theoretical for	(Co-d-alanine <sub>3</sub> )	Co-d-alanine <sub>3</sub> ). H <sub>2</sub> O
Co	18,27 %	17,30 %
N	13,00 %	12,32 %
H <sub>2</sub> O		5,28 %
Observed: $\alpha$ -salt: 17,73 % Co; 12,04 % N, 12,09 % N; 5,34 % H <sub>2</sub> O.		
,, $\alpha'$ -salt: 18,66 % Co; 12,64 % N, 12,67 %; for dried salt		
(constant at 145°—150°).		

From these data, of which the estimation of nitrogen is especially a very delicate test in this case, it is seen, that both salts are trialanine-complexes, differing only in degree of hydratation. Cryo-

scopic measurements of the molecular weight of the  $\alpha'$ -salt, which is in fact the only new, as it were anomalous product gave values, which are in accordance with mononuclear constitution, viz. theoretical value for (Co-d-alanine)<sub>2</sub> 323; observed: 295, 293, 291.

In addition it may be pointed out, that the colours of the  $\alpha$ - and  $\alpha'$ -salts, as well as their stability with respect to sulphuric acid, would neither for the  $\alpha$ -, nor for the  $\alpha'$ -complex justify the assumption of bi- or polynuclear structures e. g. of the type:



or some analogous formulae.

It may be observed, that  $\alpha'$  is not changed into  $\alpha$ -salt by drying, corresponding to an equation:



It must, therefore, be concluded that the  $\alpha$  and  $\alpha'$ -compounds are no other than the partially asymmetrical antipodes: d-[Co-d-Alan<sub>2</sub>] and l-[Co-d-Alan<sub>2</sub>], a relatively asymmetrical synthesis of such inorganic complexes thus being realized in this case. We shall in this paper only make some short remarks to support this view.

As long ago as 1920<sup>1)</sup> the author has pointed out, that when an inorganic complex is synthesized from a coloured inactive metal-salt and a colourless active molecule as the coordinated component, a relatively asymmetrical synthesis may be expected. Indirectly in that and a following paper<sup>2)</sup> this view was proved by measurements of the rotatory dispersion. The same conclusion was drawn independently by A. P. SMIRNOFF<sup>3)</sup>. A direct proof could only be offered by the isolation of the two partially asymmetrical antipodes, though, of course, it is not necessary, that both should be formed to an appreciable amount. When a compound  $d\text{I}-\text{A}$  reacts with, say  $d-\text{B}$ , a priori the compounds  $d-\text{A}-d-\text{B}$  and  $l-\text{A}-d-\text{B}$  may be expected, the ratio of  $d-\text{A}-d-\text{B}/l-\text{A}-d-\text{B}$  depending firstly on the velocity of the reactions and secondly on the possibility of inversion of  $d-\text{A}$  into  $l-\text{A}$ , and vice versa. Active compounds, which for some reasons, exhibit a strong tendency to racemisation, and therefore to inversion, may, solely for this reason, react to give exclusively  $d-\text{A}-d-\text{B}$ , or  $l-\text{A}-d-\text{B}$ . With organic compounds these phenomena are perhaps more familiar. It is, therefore, only a matter of pure chance, to find reactions leading to both

<sup>1)</sup> Zeitschr. f. wiss. Photogr. l.c.

<sup>2)</sup> Zeitschr. f. physikal. Chem. 105, 27 (1923).

<sup>3)</sup> Helv. 3, 177 (1920).

$d-A-d-B$  and  $l-A-d-B$  at the same time. In the case of our complex salts, the very great stability of the trialanine-cobaltic salts may be the cause for this way of the reaction. But even under these favourable conditions, the isolation of both the partially asymmetrical antipodes would remain impossible if they were both perfectly or practically insoluble in the solvent used. Now this must be the case with the  $\beta$ -cobaltitrialanine, which has been obtained in one form only. The correctness of this view can directly be recognized from the curves on fig. 1.

In the first place it will be seen, that the rotation curves of the  $\alpha$ - and  $\beta$ -*d-trialanine-cobaltic* salts are of so different a type, as by no means could be expected in the case of purely geometrical stereoisomerides. As the absorption-curves of both isomerides, though by no means identical, are commonly very much analogous, it might be expected, that the rotation-curves would be different only or chiefly in a quantitative way. Moreover, the  $\beta$ -curve is clearly the superposition of two curves of the type discovered by COTTON. If one of these two is supposed to be really analogous to the  $\alpha$ -curve, then it might be expected that the second curve should exhibit a relatively strong laevo-rotation in the red and a relatively small dextro-rotation in the blue part of the spectrum. That is to say, this curve would be of precisely the same type as the  $\alpha'$ -curve, which is in remarkable accordance with our views.

With respect to the  $\alpha$ - and  $\alpha'$ -salts, it must be borne in mind, that also two *racemic  $\alpha$ -trialanine-cobaltic* salts must exist, viz. *d-alanine-d-cobaltic* + *l-alanine-l-cobaltic* salt, and *d-alanine-l-cobaltic* + *l-alanine-d-cobaltic* salt, one of these being probably much more soluble in water than the other. Perhaps LEY succeeded to isolate both of them in the form of his different hydrates, without understanding the reason of their occurrence. At any case, it is worth while, to investigate the rac. complex salts of *alanine* with cobalt, from the view point mentioned above.

Summarizing, the results communicated in this paper seem to indicate a direct proof of a relatively asymmetrical synthesis of complex cobaltic salts, occurring if they are prepared from an inactive metal-salt and active coordinating molecules. Full discussion of the curves of rotatory dispersion, as well of the importance of the possibility of getting active complex salts, will be given in a separate paper on rotatory dispersion.

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**Zoology.** — “Notes concerning the variability and the action of environmental influences on the structure and growth of the Hydroid-colony *Bougainvillia ramosa* (v. Ben.) Lesson, and its bearing on systematics”. By R. BRINK. (Communicated by Prof. J. F. VAN BEMMELEN).

(Communicated at the meeting of September 27, 1924).

The number of Hydroids, which are considered as well defined species, has become enormous and the systematic literature on this group of Coelenterates has grown to a great extent. From the beginning much space in this literature has been occupied by discussions on the greater or lesser value, which is to be ascribed to certain features, for classification in larger groups. Concerning the characters for specific distinction matters stand otherwise. After the example of authorities, like ALLMAN, a.o., these characteristics (which were often based on the “habitus”), mentioned in the original speciesdiagnoses, passed from author to author without criticism, as being equal in value. Everyone confined himself to remark, that perhaps many of the forms mentioned would turn out not to represent “true species”. Nobody, however, endeavoured to distinguish genetically constant differences from such, which are due to the variability of certain habitual features under environmental influence, and to which all systematic-specific importance must be denied. Yet H. DRIESCH<sup>1)</sup> has already emphasized the fact that the mode of growth and ramification, and, in consequence, the structure and “habitus” of the Hydroid-colony, are determined by two different factors, which should be strictly kept asunder. The first factor is a certain regularity of ramification, peculiar to different groups, (DRIESCH’s “Wachstumsgesetz”), which is rightly considered as important for systematic interpretation. (It should only be remembered that for *Athecata* in general a “racemous”, for *Thecata* a “cymous” ramification is characteristic). The other factor is the strongly modifying influence of environmental differences, which is of special importance in the case of Hydroids.

This weak point of Hydroid-systematics is due to the fact that

<sup>1)</sup> Jen. Ztschr. f. Naturw. XXIV, (1890).



the study of the variability of external features has not kept pace with the discovery and the description of new forms. How important an adequate critical study (which to a great extent can consist in mere literary research), regarding the sphere of variability of certain "specific" qualities, may prove for systematics, is shown by the work of A. FENCHEL<sup>1)</sup>. Based on a research of this nature, this author succeeded in proving that 22 *Tubularia*-forms, described as new species, all belong to the species *T. larynx* Ell. et Sol., which Hydroid shows a high variability in many respects.

Reliable data, communicated in literature, regarding the causal relation between certain environmental factors and the appearance of certain peculiarities in the structure of these varying species, are still scarcer than those on the mere extent of the variability.

Attention must be paid to some remarks made on this subject by HJ. BROCH<sup>2)</sup>, who is looked upon as an authority in modern Hydroidology:

(from „Vorwort“) „Das Variationsvermögen der einzelnen Individuen ist auffällig, und es ist deswegen sehr merkwürdig, dass niemand bisher versucht hat, die Variationsverhältnisse der Arten systematisch auseinanderzusetzen.“

(pag. 136) „Es ist noch nicht in dieser Gruppe untersucht worden, ob die Arten mit den äusseren, physischen Verhältnissen parallel variabel seien.“

(pag. 135) „Die Hydroiden sind vielleicht durchgehend in höherem Grade als die Arten der meisten sonstigen Tiergruppen sehr grossen und weitgehenden individuellen Variationen unterworfen,“ . . .

. . . „Die individuellen Variationen sind vielgestaltig und mit unseren jetzigen Kenntnissen derselben und ihrer Ursachen sehr rätselhaft. Ein Zusammenhang der Variationen und der geographischen oder anderen Verhältnisse wurde in einigen wenigen Fällen nachgewiesen; meistens aber scheinen die Variationen zufällig und völlig unregelmässig zu sein.“ . . .

. . . „Es musz deswegen künftigen Untersuchungen vorbehalten sein, Licht in jene Verhältnisse zu werfen, die die individuellen Variationsrichtungen der Hydranthen und die Verhältnisse der Variationen überhaupt bedingen.“

My observations were made in the Zoological Station at Helder, on a large quantity of living material, belonging to a remarkable Hydroid "species": *Bougainvillia benedenii* Bonnevie, of which few

<sup>1)</sup> Rev. Suisse de Zool. 13, (1905).

<sup>2)</sup> Fauna Arctica V (1), (1910).

and incomplete data are to be found in literature. By comparison with material of *Bougainvillia ramosa* (v. Ben.) Lesson from Naples and from the Zuiderzee <sup>1)</sup> and also by literary study on some other allied forms, I was led to certain conclusions, regarding the specific value of the features which are taken into consideration when defining several *Bougainvillia*-species. Besides I was able to study the influence of environmental factors on them. Some of these features, which apparently represent essential points of difference between *B. ramosa* and certain other so-called species, especially deserve our attention, and the more so as in the most recent systematic Hydroid-literature (e. g. in E. STECHOW's papers <sup>2)</sup>) great specific importance is ascribed to those peculiarities, according to my opinion wrongly. I must confine myself here to a short resumption of results. For a detailed description and argumentation I must refer to a memoir with figures and complete literature- and synonym-lists, which before long, I hope, will appear in the Tijdschrift der Nederlandsche Dierkundige Vereeniging.

In living material of *B. benedenii* Bonnev. I observed some peculiarities, not noted there before, which are mentioned by ALLMAN as being of specific differential value for his *B. "fruticosa"*. Therefore I felt the desirability of looking up other points of agreement between this latter species and *B. benedenii*, and began by consulting the literature after ALLMAN's works. The result was rather surprising. It turned out soon, that the most characteristic feature of *B. benedenii*, the occurrence of enigmatical long and filiform appendages, scattered in great number along the entire hydrocaule, in which KRISTINE BONNEVIE <sup>3)</sup> found the principal reason for defining this form as an apart species, is mentioned by O. HAMANN <sup>4)</sup> as being a characteristic of his specimens of *B. "fruticosa"* Allm., and by E. GRAEFFE <sup>5)</sup> it is also mentioned for his colonies of *B. "musculus"* Allm. In the same way, by comparing other and independent notes, it could successively be proved that all distinguishing features between the above mentioned three forms do not possess any specific value, though these three forms in their extreme condition may easily lead to the false conclusion that they belong to quite different species. Two of these features, seemingly

<sup>1)</sup> The latter, belonging to the material of the Zuiderzee-monograph, was sent to me for closer examination by Dr. H. C. REDEKE, to whom I wish to acknowledge here my indebtedness for his kindness.

<sup>2)</sup> Zool. Jahrb. (Syst.) 42, (1920), p. 25—27, and ibid. 47, (1923), p. 60, 78.

<sup>3)</sup> Z. f. Wiss. Zool. 63, (1898).

<sup>4)</sup> Jen. Zeitschr. f. Nat. XV, (1882).

<sup>5)</sup> Arb. Zool. Inst. Wien, 5, (1884).

quite independent from each other, show a remarkable relation, when their morphological and physiological significance is taken into consideration, (on which in the systematic literature only few and vague suppositions are found), and when they are considered in relation with certain influences of the surrounding medium. Moreover they represent points of contact and agreement with *B. ramosa* (v. Ben.) Lesson. The characters meant are: 1. the poly- or monosiphonic structure of the stem and its principal branches, and 2. the presence or absence of the above-mentioned filiform appendages.

1. The different categories of polysiphonic structure, which occur in several Hydroid-colonies, agree in this point, that the principal stem of the colony, which by its peridermsheath is inhibited from growing in thickness, increases in solidity by the joining together of parallel stolons. This character is conspicuous in a tall, regularly and widely ramified *B. ramosa*-colony from Naples, whose stem, ramified according to the principle of a "monopodium with terminal hydranth and intercalair growth", is surrounded and overgrown by a great number of aggregated supporting tubules. As these supporting stolons strictly follow the stem and branches, against which they are tightly pressed, the above-mentioned regular racemous structure of the colony remains intact. In contradiction with the statements of H. DRIESCH (l.c.) I was able, by cautiously loosening those parallel stolons, to show that they give birth to hydranths along their sides, and in consequence their function is not exclusively a fortifying one. Small *ramosa*-colonies less clearly show this kind of polysiphonism, (which might be better indicated by the name „perisiphonism", used by A. KÜHN). The still more minute and irregularly branched colonies of *B. "fruticosa"* and *B. benedenii* possess but few of such supporting stolons, which besides do not regularly run parallel to each other, but are often twisted together. In some cases the stems and branches are found entirely without them, and consequently are monosiphonic. For the almost unbranching and dwarfish *B. "muscus"* Allm. a monosiphonic stem is mentioned by ALLMAN as giving off a typical specific character. After the foregoing it may be considered probable, however, that the poly-, or monosiphonic condition depends directly on the mechanical claims to which the stem has to respond, in which a principal part is played by the environment. With this opinion the account of Mme. S. MORZ—KOSSOWSKA<sup>1)</sup> is in agreement, who, basing herself on the observation that the shorter specimens of her *B. ramosa*-colonies are monosiphonic,

<sup>1)</sup> Arch. Zool. Exp. et Gén. IV (3), (1905).



and pass gradually, without limits, to the "type" of *B. "muscus"* Allm., regards these two forms as belonging to the same species.

2. The morphological and physiological significance of the enigmatic filiform appendages, which would represent the most important specific character of *B. "benedenii"*, is explained by A. BILLARD<sup>1)</sup>. Based on the close examination of these, and many other aberrant branches, resembling them (e.g. of *Campanularia angulata* Hincks), he showed that they are freehanging stolons, which, however, when coming into contact with foreign objects, may attach themselves to them, grow out and give origin to new colonies by forming buds at their sides. In this way they show a remarkable analogy to the offshoot of strawberryplants; their function is a certain mode of multiplication of colonies. Though, according to my opinion, BILLARD is right, when he considers the phenomenon of "secondary scissiparity" (which, following up his description, occurs in a few other species of Hydroids, and which consists in the sudden breaking off of larger or smaller parts of these "stolonic branches", generally before the latter have been able to attach themselves), as being caused by the action of environmental influences (agitated water), he does not pay any attention to the possibility, that certain influences of the environment may directly cause the appearance of such "stolonic branches". On the contrary he considers this feature as a constant specific quality. He notes that the species which show "stolonic branches", for the greater part occur in localities where the water is always in strong motion, and the circumstances are favorable to this manner of multiplication. These "stolonising species"<sup>2)</sup>, according to him, would, in consequence, be indirectly adapted in this respect. This opinion, however, does not hold good at least for *Bougainvillia*.

P. HALLEZ<sup>3)</sup> published a very short note, concerning the relation between *B. "fruticosa"* Allm. and *B. ramosa*, which is highly important here. Some parts of typical, regularly branched *B. ramosa*-colonies, which had been kept in an aquarium, in which the water was continuously in a state of violent movement, had undergone

<sup>1)</sup> Ann. Sc. Nat. (8), XX, (1904).

<sup>2)</sup> The denominations „stolonisation" and „rameaux stoloniques" used by BILLARD, are confusing, as there are more and quite different modes of stolonisation. One may compare the above described perisiphonism and also the creeping, filiform stolons at the hydrorhiza of the most Hydroidcolonies. B. has exclusively in view one special mode of stolonisation, viz. the presence of these free-hanging stolonic branches for the multiplication of the colonies.

<sup>3)</sup> C. Rend. Ac. Sc. Paris, 13 févr. 1905.



considerable changes. After some time they bore large numbers of "stolonic branches" (in the sense of BILLARD), and for the rest, as regards irregularity of ramification, shape of hydranths, arrangement of medusa-buds, etc. were quite indistinguishable from the typical *B. "fruticosa"* Allm., of which HALLEZ could dispose of material for comparison. Consequently he does not hesitate to consider the latter as being a "facies d'eau agitée" of *B. ramosa*. The description, given by H. of this "*fruticosa*" form, agrees, up to the minutest details, with my material of *B. "benedenii"* Bonnef., and the spot where the latter was found, a raft in the port of Nieuwediep, being characterized by an extremely strong tide-stream, supports the above-mentioned view.

We noted, that all distinguishing characteristics between the three so-called species: *B. "musculus"* Allm., *B. "fruticosa"* Allm. and *B. "benedenii"* Bonnef. do not bear specific value and we are now entitled to add that these forms all represent environmental races of *B. ramosa* (v. Ben.) Lesson, the latter species possessing a high variability in several features. *B. "benedenii"* bearing much resemblance to *B. "fruticosa"*, is like the latter a form in which *B. ramosa* presents itself in localities where a violent stream occurs, by whose immediate influence its characteristic structure is caused.

Considered from this point of view the differences between the three forms are rather easily understood. The perisiphonism of the stem and principal branches in the "typical" *ramosa*, and the occurrence of filiform appendages in "*benedenii*" are nothing but two different manifestations of the same original feature, consisting in the formation of stolons or stolon branches, which, under various external influences, are used in quite different ways. According to this, P. HALLEZ (l.c.) is really wrong when he states that the typical *ramosa*-colonies do not show stolonisation.

*B. ramosa* from calm, deep waters is very tall (attaining a height of about four inches) and wide-spreading; the stem in relation with this habitus is strongly supported by large numbers of parallel stolons; the branches are slender and start at nearly right angles. The hydranths, being sensible to the slightest irritation, show a high degree of retractability and in this regard contrast with the remarkable oblong-cylindrical and less-retractile hydranths of "*benedenii*", which are, so to say, accustomed to continual disturbance. The mode of ramification is regularly monopodial with terminal hydranth and intercalair growth; the branches of the 1st order show a rate of growth which is about equal to that of the stem

and, as they are younger than the latter, they therefore remain shorter. The branches of the 2<sup>nd</sup> order in most cases bear ramules with hydranths, which in their turn do not show further ramification.

By this mode of growth and ramification the older hydranths, provided with meduse-buds at their ramules, are always standing at the extremity of the colony, on the top of a branch.

It is evident, however, that a colony of this kind, is able to maintain itself in this shape only in a calm medium, on great depths for instance. In localities with torrential water the same hydroid must be quite differently shaped. The top is forced into the direction of the stream. The branches are crowded together and pressed against the stem, and the hydranths and branches of 2<sup>nd</sup> order, placed at the inner side of the branches of 1<sup>st</sup> order, are cornered. In this way the regularity of the monopodial growth is lost; certain branches are hindered in growth; others, on the contrary, relatively grow even quicker than the principal stem. At several points there exists, in consequence, a transition from monopodial to sympodial growth and in several ways there is produced the possibility that older branches and hydranths seem to have budded from others, which in reality are younger and morphogenetically are of a higher order. As this is not confined to certain rules, one gets the habitus, typical for "*fruticosa*" and still more for "*benedenii*", consisting in irregular branching of densely crowded colonies, showing further the older hydranths with meduse-buds (or meduse-buds only) not only at the periphery, but scattered over the whole colony, even more proximately along the branches. Many specimens, accounted for as being *B. ramosa*, show branches, given off at sharper angles with the principal stems and equally in other respects are less resembling the above described "calm-water-form". This can be stated with certainty of the *ramosa*-material from the Zuiderzee, which is really quite equal to "*fruticosa*", after ALLMAN's descriptions, and represents an intermedial form between the "calm-water-form" and "*benedenii*". As the colonies have smaller dimensions, a thick, perisiphonic stem is not necessary. The stem must be proof rather against stretching than bending. The supporting stolons, showing sidebranches or hydranths, are few in number and running irregularly, more twisting, along the stem (this was also obvious in the *Zuiderzee-ramosa*-material) and at some points they get apart from the stem. The step from such a colony to "*benedenii*", with free-hanging stolons, which may entirely detach themselves by breaking off from the colony, and give origin to new colonies elsewhere, is an easy one.

These stolonie branches seem to introduce into the colony a new principle of growth, consisting in terminal prolongation and giving off buds at their sides, contrasting with the typical intercalair growth with terminal hydranth. In reality, however, this principle is not at all new; it is found as well in the typical *ramosa* (in the supporting stolons) but is more hidden there and the typical racemously branched appearance is not noteworthily influenced by it.

It stands to reason that we are still far from having a clear idea concerning the true nature of the action of the environment on all the characteristic features by which the above named *Bougainvillia*-forms are distinguished from each other. It is to be stated as certain, however, that those points of difference may be directly caused by external influences, and consequently should not be used as characteristics of specific value.

Finally it seems to me not quite improbable that many other "stolonising species", mentioned by BILLARD, might equally be nothing more than environmental races of species which in other localities do not show the phenomenon pointed out by him, or do so in another way, and which therefore are still considered as representing apart species.

Groningen, September 1924.

From the Zoological Laboratory  
of the University.

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**Mathematics.** — “*Ueber projektive Differentialinvarianten*”. I.  
Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of October 25, 1924).

§ 1.

Es seien  $t_1, t_2, \dots, t_m$   $m$  komplexe Parameter und

$$y_i = y_i(t_1, t_2, \dots, t_m) \quad (i = 1, 2, \dots, n), \quad n \geq m-2, \quad m \geq 1 \dots (1)$$

die projektiven Koordinaten eines Punktes  $y$  eines  $m$ -dimensionalen, i. A. nicht linearen Raumes in einem projektiven Raume von  $n-1$  Dimensionen ( $n \geq 2$ ).

Wir betrachten in diesem Punkte  $y$  ganze rationale, geometrische, projektive Differentialinvarianten  $f$ . Das sind Polynome

$$f = f\left(y_i, \frac{\partial y_i}{\partial t_\alpha}, \frac{\partial^2 y_i}{\partial t_\alpha \partial t_\beta}, \dots\right) \dots \dots \dots (2)$$

mit den nachfolgenden drei Eigenschaften:

1. *Eigenschaft G.* Bei einer projektiven Transformation der Punkte  $x$  des  $(n-1)$ -dimensionalen Raumes

$$X_i = a_{1i}x_1 + a_{2i}x_2 + \dots + a_{ni}x_n \quad |a_{ik}| \neq 0, \dots \dots (3)$$

haben wir für das transformierte  $f$ :

$$F = f\left(Y_i, \frac{\partial Y_i}{\partial t_\alpha}, \dots\right) = |a_{ik}|^q f \dots \dots \dots (4)$$

Hieraus folgt nach einem bekannten Satze aus der Theorie der projektiven Invarianten, dass  $f$  ein Polynom von Klammerfaktoren ist. Ein Klammerfaktor ist eine  $n$ -reihige Determinante der Gestalt

$$(y_\alpha y_\beta \dots y_\epsilon) = \begin{vmatrix} y_{1,\alpha} & y_{2,\alpha} & \dots & y_{n,\alpha} \\ y_{1,\beta} & y_{2,\beta} & \dots & y_{n,\beta} \\ \dots & \dots & \dots & \dots \\ y_{1,\epsilon} & y_{2,\epsilon} & \dots & y_{n,\epsilon} \end{vmatrix} \dots \dots \dots (5)$$

Hierin bedeuten  $\alpha, \beta, \dots$  Ableitungen von  $y_i$  nach der Parameter  $t$ .





In (7) ist  $\varphi\left(\lambda, \frac{\partial \lambda}{\partial t_i}, \dots\right)$  ein Polynom. Ersetzen wir in

$$\tilde{f} = f(\lambda y, \dots) = \varphi(\lambda, \dots) \cdot f(y, \dots)$$

$\lambda y$  durch  $\eta$ , dann ist

$$f(\eta, \dots) = \varphi(\lambda, \dots) \cdot f\left(\frac{\eta}{\lambda}, \dots\right).$$

Wegen (7) haben wir aber:

$$f\left(\frac{\eta}{\lambda}, \dots\right) = \varphi\left(\frac{1}{\lambda}, \dots\right) \cdot f(\eta, \dots).$$

Daher wird

$$f(\eta, \dots) = \varphi(\lambda, \dots) \cdot \varphi\left(\frac{1}{\lambda}, \dots\right) \cdot f(\eta, \dots)$$

oder, da  $f \equiv 0$  ist:

$$\varphi\left(\lambda, \frac{\partial \lambda}{\partial t_i}, \dots\right) \cdot \varphi\left(\frac{1}{\lambda}, \frac{\partial}{\partial t_i}\left(\frac{1}{\lambda}\right), \dots\right) = 1.$$

Hieraus für jedes  $\lambda$ :

$$\varphi\left(\lambda, \frac{\partial \lambda}{\partial t_i}, \dots\right) \cdot \psi\left(\lambda, \frac{\partial \lambda}{\partial t_i}, \dots\right) = \lambda^s \dots \dots \dots (14)$$

wo  $\psi$  wieder ein Polynom. Daher ist  $\varphi$  eine Potenz von  $\lambda$ .

Die Gleichung (12) kann man so beweisen wie den entsprechenden Satz bei linearen Transformationen (3). In

$$\bar{f} = \Phi\left(\frac{\partial t_i}{\partial t_\alpha}, \frac{\partial^2 t_i}{\partial t_\alpha \partial t_\beta}, \dots\right) \cdot f \dots \dots \dots (15)$$

is  $\Phi$  eine ganze rationale Funktion. Wegen  $\Delta \neq 0$  existiert die mit (9) inverse Transformation

$$\bar{t}_i = \bar{t}_i(t_1, t_2, \dots, t_m) \dots \dots \dots (16)$$

und gibt, angewendet auf  $\bar{f}$ , die Gleichung

$$f = \Phi\left(\frac{\partial \bar{t}_i}{\partial t_\alpha}, \dots\right) \cdot \bar{f}.$$

Multiplizieren wir dies mit (15), so haben wir

$$\Phi\left(\frac{\partial t_i}{\partial t_\alpha}, \dots\right) \cdot \Phi\left(\frac{\partial \bar{t}_i}{\partial t_\alpha}, \dots\right) \equiv 1. \dots \dots \dots (17)$$

Sei  $\Delta_i^\alpha$  der Minor von  $\frac{\partial t_i}{\partial t_\alpha}$  in  $\Delta$ , also

$$\Delta_i^\alpha = \frac{\partial \Delta}{\partial \frac{\partial t_i}{\partial t_\alpha}},$$

dann ist

$$\frac{\partial \bar{t}_i}{\partial t_\alpha} = \frac{\Delta_\alpha^i}{\Delta} \quad \dots \quad (18)$$

und  $\Delta_\alpha^i$  ist eine ganze rationale Funktion von ausschliesslich ersten Ableitungen  $\frac{\partial t_\lambda}{\partial t_\mu}$ . Aus (18) folgt dann wegen

$$\frac{\partial^2 \bar{t}_i}{\partial t_\alpha \partial t_\beta} = \sum_\lambda \frac{\partial \left( \frac{\Delta_\alpha^i}{\Delta} \right)}{\partial t_\lambda} \frac{\partial \bar{t}_\lambda}{\partial t_\beta} = \sum_\lambda \frac{\partial \left( \frac{\Delta_\alpha^i}{\Delta} \right)}{\partial t_\lambda} \frac{\Delta_\beta^\lambda}{\Delta}$$

dass

$$\frac{\partial^h \bar{t}_i}{\partial t_\alpha \partial t_\beta \dots \partial t_\gamma} = \frac{1}{\Delta^s} \cdot G \left( \frac{\partial t_i}{\partial t_\alpha}, \frac{\partial^2 t_i}{\partial t_\alpha \partial t_\beta}, \dots \right)$$

ist, wobei  $G$  wieder ein Polynom bedeutet. Nach (17) haben wir also:

$$\Phi \left( \frac{\partial t_i}{\partial t_\alpha}, \dots \right) \cdot \Psi \left( \frac{\partial t_i}{\partial t_\alpha}, \dots \right) = \Delta^s \quad \dots \quad (19)$$

wo auch  $\Psi$  wieder ein Polynom. Hieraus folgt  $\Phi = \Delta^s$ , denn erstens ist die Determinante  $\Delta$  irreduzibel und zweitens können wir in jedem Punkte  $(t_1^0, t_2^0, \dots, t_m^0)$  des  $t$ -Raumes die Ableitungen  $t_{i,\alpha}, t_{i,\alpha\beta}, \dots$  willkürlich wählen, d. h. wir können sie in (19) als unabhängige Variable betrachten.

### § 3.

Der Hauptsatz, den wir hier beweisen wollen, lautet:  
Sind

$$K_1, K_2, \dots, K_{m+2} \quad \dots \quad (20)$$

$m+2$  geometrische, projektive Differentialinvarianten mit den  $\lambda$ -Gewichten  $p_1, p_2, \dots, p_{m+2}$  und mit den  $\Delta$ -Gewichten  $q_1, q_2, \dots, q_{m+2}$ , dann ist die Determinante

$$\{K_1, K_2, \dots, K_{m+2}\} = \begin{vmatrix} p_1 K_1 & p_2 K_2 & \dots & p_{m+2} K_{m+2} \\ q_1 K_1 & q_2 K_2 & \dots & q_{m+2} K_{m+2} \\ \frac{\partial K_1}{\partial t_1} & \frac{\partial K_2}{\partial t_1} & \dots & \frac{\partial K_{m+2}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_1}{\partial t_m} & \frac{\partial K_2}{\partial t_m} & \dots & \frac{\partial K_{m+2}}{\partial t_m} \end{vmatrix} \quad (21)$$

eine Invariante mit dem  $\lambda$ -Gewicht  $p = 1 + p_1 + \dots + p_{m+2}$  und mit dem  $\Delta$ -Gewicht  $q = 1 + q_1 + \dots + q_{m+2}$ .

Wir beweisen diesen Satz in drei Schritten.

1. Sind  $K_1, K_2, \dots, K_m$   $m$  absolute projektive Differentialinvarianten d. h. solche mit den Gewichten Null, dann ist die Funktionaldeterminante

$$D = \frac{\partial (K_1, K_2, \dots, K_m)}{\partial (t_1, t_2, \dots, t_m)} = \begin{vmatrix} \frac{\partial K_i}{\partial t_k} \end{vmatrix} \dots \dots \dots (22)$$

eine Invariante mit  $\lambda$ -Gewicht Null und mit  $\Delta$ -Gewicht 1.

Bei der Transformation

$$t_i = t_i(\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m)$$

erhalten wir nämlich aus

$$\bar{K}_i = K_i \quad (i = 1, 2, \dots, m)$$

durch Anwendung des Multiplikationssatzes für Determinanten:

$$\bar{D} = \frac{\partial (\bar{K}_1, \bar{K}_2, \dots, \bar{K}_m)}{\partial (\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m)} = \frac{\partial (K_1, K_2, \dots, K_m)}{\partial (t_1, t_2, \dots, t_m)} \cdot \frac{\partial (t_1, t_2, \dots, t_m)}{\partial (\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m)},$$

also:

$$\bar{D} = D \cdot \Delta \quad \dots \dots \dots (23)$$

2. Sind  $K_1, K_2, \dots, K_{m+1}$   $m+1$  projektive Differentialinvarianten mit den  $\lambda$ -Gewichten Null und den  $\Delta$ -Gewichten  $q_1, q_2, \dots, q_{m+1} \neq 0$ , dann ist die Determinante

$$T = \begin{vmatrix} q_1 K_1 & q_2 K_2 & \dots & q_{m+1} K_{m+1} \\ \frac{\partial K_1}{\partial t_1} & \frac{\partial K_2}{\partial t_1} & \dots & \frac{\partial K_{m+1}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_1}{\partial t_m} & \frac{\partial K_2}{\partial t_m} & \dots & \frac{\partial K_{m+1}}{\partial t_m} \end{vmatrix} \quad \dots \dots (24)$$



eine Differentialinvariant mit  $\lambda$ -Gewicht Null und mit  $\Delta$ -Gewicht  $1 + q_1 + q_2 + \dots + q_{m+1}$ .

*Beweis.* Es ist  $q_{m+1} \neq 0$ ; deshalb sind

$$\frac{\frac{K_1}{q_1}}{K_{m+1}^{q_{m+1}}}, \frac{\frac{K_2}{q_2}}{K_{m+1}^{q_{m+1}}}, \dots, \frac{\frac{K_m}{q_m}}{K_{m+1}^{q_{m+1}}} \dots \quad (25)$$

$m$  absolute Invarianten, worauf wir den vorigen Satz anwenden können. Es ist also

$$\text{Det.} \left| \frac{\partial}{\partial t_k} \left( \frac{\frac{K_i}{q_i}}{K_{m+1}^{q_{m+1}}} \right) \right|$$

eine relative Invariante mit dem  $\Delta$ -Gewicht 1. Daher hat

$$\begin{aligned} \text{Det.} \left| \frac{\partial K_i}{\partial t_k} \frac{K_{m+1}^{-q_{m+1}}}{K_{m+1}^{q_{m+1}}} - \frac{q_i}{q_{m+1}} \frac{K_{m+1}^{-q_{m+1}-1}}{K_{m+1}^{q_{m+1}}} \cdot \frac{\partial K_{m+1}}{\partial t_k} \cdot K_i \right| = \\ = K_{m+1}^{-m} \frac{q_1 + \dots + q_m}{q_{m+1}} \cdot \text{Det.} \left| \frac{\partial K_i}{\partial t_k} \cdot K_{m+1} - \frac{q_i}{q_{m+1}} \frac{\partial K_{m+1}}{\partial t_k} \cdot K_i \right| \end{aligned}$$

das  $\Delta$ -Gewicht 1, oder

$$\text{Det.} \left| \frac{\partial \left( \frac{1}{q_i} K_i \right)}{\partial t_k} \cdot K_{m+1} - \frac{\partial \left( \frac{1}{q_{m+1}} K_{m+1} \right)}{\partial t_k} \cdot K_i \right| \dots \quad (26)$$

hat das  $\Delta$ -Gewicht  $1 + (q_1 + \dots + q_m) + mq_{m+1}$ .

Rändern wir diese Determinante (26) mit einer ersten Zeile

$$K_1, K_2, \dots, K_{m+1}$$

und  $K_{m+1}, 0, 0, \dots, 0$  als letzten Kolonne, so ergibt eine einfache Umformung den Satz (24).

3. *Beweis des Hauptsatzes.* Es sei  $p_{m+2} \neq 0$ . Dann sind

$$\frac{\frac{K_1}{p_1}}{K_{m+2}^{p_{m+2}}}, \frac{\frac{K_2}{p_2}}{K_{m+2}^{p_{m+2}}}, \dots, \frac{\frac{K_{m+1}}{p_{m+1}}}{K_{m+2}^{p_{m+2}}} \dots \quad (27)$$

$m+1$  Invarianten mit den  $\lambda$ -Gewichten Null und den  $\Delta$ -Gewichten

$$q_h - q_{m+2} \frac{p_h}{p_{m+2}}, \quad (h = 1, 2, \dots, m+1).$$

Auf diese Invarianten (27) ist daher der vorige Satz anwendbar und ergibt die folgende Invariante, wobei wir nur das erste und das  $(i+1)$ -te Element der  $h$ -ten Kolonne anschreiben:

$$T = \begin{vmatrix} \dots & \frac{q_h p_{m+2} - p_h q_{m+2}}{p_{m+2}} K_h & \frac{p_h}{K_{m+2}^{p_{m+2}}} & \dots \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_h}{\partial t_i} \cdot K_{m+2}^{p_{m+2}} & -\frac{p_h}{p_{m+2}} \cdot \frac{\partial K_{m+2}}{\partial t_i} \cdot K_h & -\frac{p_h}{K_{m+2}^{p_{m+2}}} - 1 & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

In  $T$  multiplizieren wir zuerst die  $h$ -te Kolonne ( $h=1, 2, \dots, m+1$ ),

mit  $\frac{p_h}{K_{m+2}^{p_{m+2}}} + 1$ ; dann rändern wir mit einer ersten Zeile

$$p_1 K_1, p_2 K_2, \dots, p_h K_h, \dots, p_{m+1} K_{m+1}, p_{m+2} K_{m+2}$$

und erhalten die Invariante:

$$T'' = \begin{vmatrix} \dots & p_h K_h & \dots & p_{m+2} K_{m+2} \\ \dots & (q_h p_{m+2} - p_h q_{m+2}) K_h K_{m+2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ \dots & p_{m+2} \frac{\partial K_h}{\partial t_i} K_{m+2} - p_h K_h \frac{\partial K_{m+2}}{\partial t_i} & \dots & 0 \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

Hier multiplizieren wir die erste Zeile mit  $q_{m+2} K_{m+2}$  und addieren dies zur zweiten Zeile; dann multiplizieren wir die erste Zeile mit  $\frac{\partial K_{m+2}}{\partial t_i}$  und addieren dies zur  $(i+2)$ -ten. Sondern wir dann gemeinsame Faktoren ab, so erhalten wir schliesslich (21).

Im Nachhinein sehen wir, dass (24) ein spezieller Fall von (21) ist, nämlich der, wo  $p_1 = p_2 = \dots = p_{m+1} = 0$ ,  $p_{m+2} \neq 0$  gesetzt ist. Ebenso ist (22) wieder ein besonderer Fall von (24), der entsteht, wenn wir  $q_1 = q_2 = \dots = q_m = 0$ ,  $q_{m+1} \neq 0$  setzen.

Setzen wir in (21)  $q_1 = q_2 = \dots = q_{m+1}$ ,  $q_{m+2} \neq 0$ , so erhalten wir analog (24) den folgenden Satz:

Sind  $K_1, K_2, \dots, K_{m+1}$   $m+1$  projektive Differentialinvarianten

mit den  $\lambda$ -Gewichten  $p_1, p_2, \dots, p_{m+1}$  und mit  $\Delta$ -Gewichten Null, dann ist

$$\begin{vmatrix} p_1 K_1 & p_2 K_2 & \dots & p_{m+1} K_{m+1} \\ \frac{\partial K_1}{\partial t_1} & \frac{\partial K_2}{\partial t_1} & \dots & \frac{\partial K_{m+1}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_1}{\partial t_m} & \frac{\partial K_2}{\partial t_m} & \dots & \frac{\partial K_{m+1}}{\partial t_m} \end{vmatrix} \dots \dots \dots (28)$$

eine Invariante mit dem  $\lambda$ -Gewichte  $1 + p_1 + \dots + p_{m+1}$  und mit dem  $\Delta$ -Gewichte 1.

Wir führen schliesslich noch an, dass die Klammerausdrücke (21) den folgenden Gleichungen genügen:

$$\{A, B, \dots, G+H\} = \{A, B, \dots, G\} + \{A, B, \dots, H\} \quad \dots \quad (29)$$

$$\{A, B, \dots, GH\} = \{A, B, \dots, G\} \cdot H + \{A, B, \dots, H\} \cdot G \quad \dots \quad (30)$$

$$\left\{A, B, \dots, \frac{G}{H}\right\} = \{A, B, \dots, G\} \cdot H^{-1} - \{A, B, \dots, H\} \cdot GH^{-2}. \quad (31)$$

**Chemistry.** — "*The adsorption of electrolytes on charcoal.*" By I. M. KOLTHOFF. (Communicated by Prof. H. R. KRUYT.)

(Communicated at the meeting of June 28, 1924).

1. Though numerous investigations have been described in the literature about the adsorption of electrolytes on charcoal, the explanation of this process still escapes us. On the whole electrolytes do not change the surface tension of water with regard to air — nor probably to charcoal either — or very slightly at most, so that it is not rational to explain their adsorbability by making use of the well-known theorem of GIBBS.

Another phenomenon often appears in the adsorption of electrolytes which is called "selective adsorption of ions." Charcoal often shows a preference for a particular anion or kation, if e.g. a dye-solution is shaken with charcoal, much more of the dye ion is absorbed than of the anion — or kation — with which the dye was combined<sup>1</sup>). In this so-called selective adsorption of ions the coal must send so many ions into the solution as corresponds with the difference between the quantity of adsorbed dye ion, and the other ion with which the dye ion was combined. If this were not the case the liquid would not remain electrically neutral. So we must imagine that the coal contains electrolytes as impurities, which are not easily removed, and the ions of which are able to react with other ions. Suppose e.g. a charcoal containing aluminium-silicate as an impurity we may represent the adsorption of a dye anion approximately by the following process:



The amount of dye ions taken away is replaced by an equivalent amount of silicate ions in the solution. According to this suggestion the adsorption of electrolytes is a purely chemical phenomenon, and by means of the laws of stoichiometry it is possible to deduce the formula of the adsorption isotherm, which, generally speaking, is also applicable in the adsorption of strong electrolytes.

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<sup>1</sup>) See i.a. L. MICHAËLIS and P. RONA, *Biochem. Z.* 97, 85 (1919); summary in L. MICHAËLIS: „Die Wasserstoffionenkonzentration“, 2e Aufl. 1922, p. 200 and following. HARTLEBEN: *Biochem. Z.* 115, 46 (1921).



A few years ago<sup>1)</sup> I tried to explain the phenomena in the adsorption of electrolytes on coal from a chemical standpoint. I started from the assumption that molecular adsorption of the electrolyte does not take place as such, but that the decomposition adsorption is the only phenomenon that plays a part. As, in the course of a continued investigation different facts were found which could not easily be explained from previous theories, we thought it necessary to investigate if molecular adsorption is not found with electrolytes.

2. In order to exclude decomposition adsorption it was necessary to start with charcoal of the highest purity possible, and practically free from electrolytes. It was prepared in more or less the same way as F. E. BARTELL and E. J. MILLER<sup>2)</sup> had obtained this preparate. I started from cane sugar with 0,005 % of ash. It was carefully carbonised in a platinum dish. Then the coal was heated for some days in a silica crucible, over a gasoline burner, until its appearance was no longer bright black but more or less dull. At first we admitted some air during the process of heating, which was discontinued later on. The coal thus obtained had a percentage of ash varying between 0,08 % and 0,09 %. I call attention to the fact that BARTELL and MILLER's charcoal was better, as it contained only 0,01 % of ash or even less. At any rate my charcoal was sufficiently pure for my investigation, and the conclusion which we shall discuss in the following pages — viz. that a molecular adsorption of electrolytes on charcoal is taking place — is decidedly justified.

3. When it was seen that acids were appreciably absorbed on the pure charcoal we thought it necessary to demonstrate that practically speaking as much of the kation as of the anion was withdrawn from the solution. The charcoal used in these investigations had an ash content of 0,09 %; the ash of one gram of charcoal neutralized 0,15 cc. of 0,1 N. acid (indicator methylorange); this corresponds therefore with an alcalinity of 0,015 milli-equivalents per one gr. of coal.

2 grs. of the coal was shaken with 50 cc. of solutions of hydrochloric acid of different concentrations. In the filtrate I determined by titration the concentration of the hydrogen ions, as well as of the chlorine ions; I moreover calculated from the conductivity of the filtrate the corresponding concentration of the hydrochloric acid.

<sup>1)</sup> I. M. KOLTHOFF, Koll. Z. **30**, 35 (1922).

<sup>2)</sup> F. E. BARTELL and E. J. MILLER, J. Am. Chem. Soc., **44**, 1865 (1922).

The final concentrations of hydrogen ions  $[H^+]$ , chlorine ions  $[Cl']$ , and  $[HCl]$  thus found, are seen in the following table:

Experiments with 2 gr. of charcoal and 50 cc. of solution.

Conc. of hydrochloric acid	Final conc. $[H^+]$	$[Cl']$	$[HCl]$ from $K_{18}$
0.0504 N	0.0436	0.0448	0.0440
0.0201 "	0.015	0.0159	0.0153
0.0100 "	0.0057	0.0069	0.0059
0.0050 "	0.00122	0.0022	0.00153

As is seen from the figures but little more hydrogen ions than chlorine ions are withdrawn from the solution by the charcoal. This was to be expected as the charcoal still contained some substance with an alkaline reaction (see above) which can react with the hydrogen ions, in consequence of which less mobile ions pass into the solution. In agreement with this fact we also find a value for the final concentration of the hydrochloric acid, calculated from the conductivity, which lies between the values of  $[H^+]$  and  $[Cl']$ .

From the above data we have also deduced how much  $H^+$  and  $Cl'$  were adsorbed in the different final concentrations. It was seen that in both cases the formula of the adsorption isotherm holds good:

$$\frac{x}{m} = \alpha c \frac{1}{n}$$

in which  $\frac{x}{m}$  represents the number of milli-equivalents adsorbed per one gr. of charcoal,  $c$  is the final concentration, and  $\alpha$  and  $\frac{1}{n}$  are constants.

In order to obtain further evidence of the fact that almost all the hydrochloric acid as such is adsorbed, and that there is no decomposition adsorption, I have made the following experiment. 2 grs. of charcoal was boiled for five minutes with 50 cc of 0,05 N. hydrochloric acid, during which time the water evaporated was continually replenished.

The charcoal was filtered off and washed with boiling water until the filtrate did not give any acid reaction with litmus paper. From the titration of the filtrate it was seen that in this case 1 gr. of charcoal had adsorbed 0,075 milli-equivalents of  $HCl$  (compare with the table above, referring to room temperature). This adsorbed quantity of hydrochloric acid passes but slowly into water. The charcoal was

Isotherm of  $[H^+]$ 

C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated	
0.0436	0.17	0.17	
0.015	0.13	0.13	$1/n = 0.25$
0.0057	0.109	0.102	$\alpha = 0.37$
0.00122	0.095	0.070	

Isotherm of  $Cl'$ 

C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated	
0.0448	0.14	0.137	
0.0159	0.108	0.107	$1/n = 0.24$
0.0069	0.084	0.0874	$\alpha = 0.29$
0.0022	0.0735	0.0663	

washed again several times with small quantities of boiling water, until we had obtained a filtrate of 100 cc. After cooling it had a faint acid reaction on methylorange; it was seen that one gr. of charcoal had given off 0,015 to 0,02 milli-equivalents of HCl. In order to make the charcoal quite free from hydrochloric acid, we washed it with 5 cc of 0,02 N. sodium hydroxide and afterwards with boiling water. Acid- and chloride-determination indicated that all the hydrochloric acid had been removed.

From these experiments results that the molecularly adsorbed hydrochloric acid cannot be completely removed by washing with water. This fact is of importance, as most of the investigations, described in the literature, have been made with impure charcoals which had been treated with acid. All these charcoals probably contain a certain amount of molecularly adsorbed hydrochloric acid, so that it is likely that with these charcoals results are obtained totally different from those with the pure charcoal which I used in my investigations.

4. The charcoal which I used also showed good results in the adsorption of bases. I investigated the adsorption of sodium hydroxide and of baryta.

The table given below illustrates the results obtained with sodium hydroxide:

Experiments with 2 grs. of charcoal and 50 cc. of sodium hydroxide.

Initial concentration	C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated
0.05 N	0.044	0.15	0.187
0.02 "	0.015	0.125	0.129
0.01 "	0.0067	0.082	0.080
0.005 "	0.003	0.05	0.032

$$1/n = 0.58$$

$$\alpha = 1.45$$

We see that the adsorption-isotherm is rather unsatisfactory.

On the whole there is much less adsorption of salts than of acids or bases. From the determination of the concentration of the kation and of the anion in the filtrate, and usually also of the conductivity, was shown that we have here molecular adsorption of the electrolyte, and that there is no decomposition adsorption of ions.

Contrary to the results of E. J. MILLER<sup>1)</sup>, I have never observed a marked hydrolytic adsorption, not even with salts as ammonium chloride, metheleneblue chloride, and salicilate of sodium.

In the adsorption of the strongly hydrolysed sodium salt of veronal (medinal) I found that the hydroxyl ion concentration of the solution was strongly reduced after the adsorption. In this case there was a simultaneous adsorption of the salt itself, and of the sodium hydroxide which was set free by hydrolysis.

Finally I wish to call attention to the fact that the charcoal which was used, lent itself readily to the adsorption of non electrolytes, as iodine and phenol.

5. Without speculating on the nature of molecular-adsorption of electrolytes we must assume that the electrolyte is adsorbed by the charcoal as an undissociated molecule or, according to the modern views of N. BJERRUM and others as associated ions. It is to be expected that neutral salts which diminish the electrolytic dissociation of the electrolyte, will increase the adsorbability.

It is also to be expected that the amount of adsorption is a specific property of every electrolyte. When we compare the adsorbability of two strong acids under the same circumstances the result may be totally different. From the data in the following table we

<sup>1)</sup> E. J. MILLER. J. Am. Chem. Soc., 46, 1150 (1924).



see that these views are indeed correct. In the tests I used a sugar-charcpal with 0,08 % of ash. 2 grs. of charcoal were shaken with 50 cc of 0,05 N. solution of the acid, with the neutral salt of the acid, as well as without, after which the concentration in the filtrate was determined. In the table is noted the amount of acid in milli-equivalents per one gr. of charcoal adsorbed.

The specific character of the adsorbability is seen very clearly when we compare the behaviour of nitric acid and perchloric acid. Under the same conditions the absorbability of the former is 4 times as strong as of perchloric acid, and trichloroacetic acid has a degree of adsorbability 7 times smaller than nitric acid. Phosphoric acid is practically speaking, not absorbed at all. Further we see that

2 grs. of charcoal with 50 cc. of 0.05 N. acid.

Acid used	Addition of salt	$\frac{x}{m}$ p. 1 g.
Hydrochloric acid	—	0.16
"	in 2 N KCl	0.29
Hydrobromic acid	—	0.16
"	" 1 N KBr	0.26
Hydroiodic acid	—	0.27
"	" 1 N KI	0.42
Nitric acid	—	0.28
"	" 2 N KNO <sub>3</sub>	0.53
Perchloric acid	—	0.072
Trichloroacetic acid	—	0.042
Sulphuric acid	—	0.048
Phosphoric acid	—	0.02
Oxalic acid	—	0.46
Acetic acid	—	0.51
"	" 2 N NaAc	0.55

neutral salts markedly increase the adsorbability of strong acids. In contrast with this the presence of acetate of sodium does not influence the adsorption of acetic acid. This was to be expected as the acid in 0.05 N. solution is for the greater part present in the undissociated state, so that the acetate of sodium raises the concen-

tration of the undissociated acid to a very small extent only. Finally I wish to observe that neutral salts on the whole have no influence on the adsorbability of non-electrolytes; on the contrary the adsorbability of sodium hydroxide and of salicylate of sodium is increased by the addition of neutral salts.

6. Now that we have demonstrated that electrolytes, as such, are adsorbed, and that the amount of adsorbability is a specific property of the electrolyte, it would be interesting to trace the influence of capillary-active substances, as phenol and amylalcohol, on the adsorption of electrolytes. Assuming that the adsorption is generally effected because a chemical affinity <sup>1)</sup> exists between the charcoal and the substance adsorbed, it is to be expected that capillary active substances, which are strongly adsorbed by charcoal, can replace the electrolytes. This indeed proved to be the case. The tests, the results of which are mentioned in the following table, have been made with 2 grs. of charcoal und 50 cc. of 0.05 N. solutions of electrolytes, without and with salt in absence and presence of 5 millimols of phenol or amylalcohol. (See table next page).

These figures prove that the strong electrolytes, to which, in this case also oxalic acid belongs, are practically totally removed from the charcoal by phenol. In this respect amylalcohol is less effective than phenol. The fact that we always find a small quantity of acid adsorbed when phenol is present, is to be attributed to the charcoal having a slight alkalinity. Neutral salts, as potassium, iodide, and salicylate of sodium are completely driven away from the charcoal by capillary active substances. Acetic acid, which also behaves like a capillary active substance is only partially driven away, as to be expected.

7. From the data, given in this preliminary paper, it follows that the adsorption of electrolytes in any commercial charcoal containing many impurities, is a very complex phenomenon. In the first place we have the molecular adsorption of the electrolyte, as described above. But at the same time the so called replacing adsorption appears, in which one ion can react chemically with one of the impurities of the charcoal. As both adsorptions always take place simultaneously, the results can never lead to a general conclusion. If the displacement adsorption alone is to be investigated, a capillary active substance must always be added, in order to repress completely the molecular adsorption of the electrolyte. A further investigation is

<sup>1)</sup> Cf. N. SCHILOW and L. LEPIN, Z. Physik. Chem. 104, 25, (1920).

## Influence of capillary substances on the adsorption of electrolytes.

Electrolyte used	Addition of salt	$\frac{x}{m}$ without capillary active subst.	$\frac{x}{m}$ in presence of	
			phenol	amylalcohol
Hydrochloric acid	—	0.16	0.03	0.04
"	2 N KCl	0.29	0.03	0.04
Hydrobromic acid	—	0.16	0.04	
"	N KBr	0.26	0.04	0.045
Hydroiodic acid	—	0.27	0.02	
Nitric acid	—	0.28	0.015	0.08
"	2 N KNO <sub>3</sub>	0.53	0.05	0.08
Oxalic acid	—	0.51	—	0.01
Acetic acid	—	0.51		0.23
Sodium hydroxide	—	0.035	0.00	0.01
"	2 N KCl	0.08	0.01	0.02
Potassium iodide	—	0.02	0.00	
Salicylate of sodium	—	0.042	—	0.001
"	2 N KCl	0.057	—	0.007

already being made along these lines, and I have already obtained results which clear up former anomalies. A further paper on this subject will treat this matter more exhaustively.

## SUMMARY.

1. A molecular adsorption of electrolytes takes place on pure charcoal.

2. Neutral salts increase the adsorbability of strong electrolytes.

3. Capillary active substances prevent or decrease the adsorption of electrolytes on pure charcoal.

4. A marked, so called "hydrolytic adsorption" on pure charcoal has not been observed.

5. A molecular- and an ion adsorption takes place simultaneously on charcoal with impurities. Both phenomena differ completely in nature. If adsorption of ions alone is to be investigated the addition of some capillary active substance is necessary to prevent molecular adsorption.

Utrecht, June 1924.

Pharmaceutical Labor. of the University.

**Heredity.** — "*Hereditary phenomena in family-portraits.*" By Dr.  
J. F. VAN BEMMELEN.

(Communicated at the meeting of September 27, 1924).

Among the family-portraits in my parental home I remember since my early youth a small picture, representing an elderly lady clad in a huge widows-cap. As I was told by my father it was the portrait of SUZANNA WEVERINGH, my great-grandmother, or more correctly expressed, one of my four great-grandmothers. I did not pay much attention to this painting, till an artist, who had taken a photo of it, remarked that he saw in it a striking likeness to my own face. This assertion was confirmed by all persons confronted with the portrait, and by comparing the photo of the picture with one of my own face, I could convince myself of its truth. That this likeness had never before been remarked by any one, must probably be explained by the very plausible supposition that it had gradually augmented in the course of my life, and so had only now become striking, after I had reached the same age as SUZANNA WEVERINGH when she was painted.

Some time afterwards, Jhr. Mr. Dr. E. A. VAN BERESTEYN kindly placed at my disposal a collection of 46 portrait-drawings, evidently made in the seventeenth century by a rather poor draughtsman, after family-pictures belonging to a group of seventeen interallied families. That such was the origin of this collection, I could prove for four of these drawings, as I became aware that one pair represented copies of oil-paintings in my own house, and another one had been taken from a couple of family-pictures that I found in the gallery of one of my relatives. As these four pictures were marked with the names of the people they represented, I could satisfy myself about the correctness of the names on the banderoles under the drawings, and felt justified in supposing the same to be the case with the rest of them. So I concluded that I had got before my eyes the effigies of no less than 29 of my direct forefathers, and of eleven other members of my ancestry, only six belonging to sidebranches which were not in blood-relationship with myself.

Among these direct ancestors was a picture of a clergyman, called



JUSTUS VAN DEN BOOGAERT, a calvinistic preacher living from 1623—1663 at Naarden and Utrecht, and belonging to the eighth parentation <sup>1)</sup>.

Once again a casual remark of an uninfluenced spectator directed my attention to the similarity between my face and that of JUSTUS VAN DEN BOOGAERT. That such a similarity really exists, I venture to conclude from the result of a little experiment, in which I invited different people to make an independent choice from the full collection of my family-portraits (now already amounting to more than a hundred), of those that according to their opinion showed the greatest likeness with myself. The larger majority of these unprepared and impartial spectators placed JUSTUS VAN DEN BOOGAERT and SUZANNA WEVERINGH at the top of their list.

Now, when tracing in my ancestral tree the relation in which I stood to these two ancestors, it turned out, that the line of descent between JUSTUS VAN DEN BOOGAERT and myself passed through SUZANNA WEVERINGH. Moreover it became evident, that, thanks to the above-mentioned portrait-album, I had the disposal of the portraits of the four intermediate generations, which all proved to be of the female sex, as may be seen from the following pedigree:

8 <sup>th</sup>	parentation	JUSTUS VAN DEN BOOGAERT and CATH. BROUWERS.
7 <sup>th</sup>	„	ANNA CATHARINA v. D. BOOGAERT and BERNARD DE MOOR.
6 <sup>th</sup>	„	ANNA CATHARINA DE MOOR and JAN VAN ROYEN.
5 <sup>th</sup>	„	JUSTINA CLARA VAN ROYEN and HENDRIK VERBEECK.
4 <sup>th</sup>	„	JACOBA ELISABETH VERBEECK and MAARTEN WEVERINGH.
3 <sup>rd</sup>	„	SUZANNA WEVERINGH and PIETER PAMA DE KEMPENAER.
2 <sup>nd</sup>	„	ANTOINETTE ADRIANA DE KEMPENAER and JAN FRANS VAN BEMMELEN.
1 <sup>st</sup>	„	JACOB MAARTEN VAN BEMMELEN and MARIA BOEKE.

As to portraits, the only missing links in this chain of ancestors are CATHARINA BROUWERS and JUSTINA CLARA VAN ROYEN, but I am in possession of the portraits of no less than three sisters of the latter, which all show a remarkable resemblance to one another, but have no feature in common either with JUSTUS VAN DEN BOOGAERT or with SUZANNA WEVERINGH. The origin of this family-type of the sisters

<sup>1)</sup> I have made the proposition to indicate the successive generations of ancestors by the theoretical number of their members. According to this method I call JUSTUS VAN DEN BOOGAERT my 256-father.

By an English friend and colleague, who had the kindness to correct my translation of the Dutch original, my attention was called to the fact that parentation and filiation are not habitual English expressions, but nevertheless will be understood by English scholars of genetics.

VAN ROYEN I consider to be able to trace through the paternal ancestry, as I am acquainted with the portraits of no less than eight members of that line:

CORNELIS I VAN ROYEN and PETRONELLA VAN BLANKENDAEL.

NICOLAAS VAN ROYEN and ANNA VAN SOLINGEN.

CORNELIS II VAN ROYEN and JOHANNA DE ST. GILLES.

JAN VAN ROYEN and ANNA CATHARINA DE MOOR.

From these portraits it becomes evident, that it is JOHANNA DE ST. GILLES who has imprinted her type on her descendents.

Moreover the abovenamed album (which probably has been drawn by a member of the VAN ROYEN-family, and so may be called "album-VAN ROYEN") contains the portrait of JUSTUS VAN DEN BOOGAERT's father, called GILLES, and married to CORNELIA VERSPREET, but also this does not show any striking resemblance to his son.

From these facts I conclude that the familiar type of facial features is handed down from parent to child for an undefined number of generations, without however manifestating itself in each succeeding filiation. So the repetition of the type occurs in leaps, and the number of intervening generations between each pair of manifestations cannot be predicted beforehand. It therefore becomes evident, that the type is hereditarily handed down by parents, who carried it genotypically, but did not themselves show it phenotypically.

In itself this assertion contains nothing strange or unexpected; it only teaches us that family-likeness follows the same rules as other hereditary features, mental as well as physical. My intention in this communication is simply to draw attention to the importance of portrait-studies for the knowledge of hereditary phenomena in man. An inevitable preliminary condition for this study is to get acquainted with the stock of portraits still existing. That this knowledge is far from satisfying or in any way complete, I need not specially insist upon; the majority of people possessing family-pictures are not at all or at least not correctly informed about the names of the persons represented, and many paintings have been combined in pairs, and framed anew, only to form nice decorative couples, without any regard to their real relation. Still worse are the conditions in the era of photography; the overwhelming majority of photo's are not provided with names, and consequently soon become unrecognizable. It may therefore be asserted without the least exaggeration, that nowadays the whole world becomes photographed, but no scientific result of any importance whatever comes out of this immense iconographic material of the species *Homo sapiens*.

Still one more ancestral portrait in the album-VAN ROYEN drew my particular attention: that of CLARA CLAESDOCHTER COLIJN, as so many persons, who joined in the above-mentioned experiment, placed it on their list of ancestors showing a special likeness to myself. The line of blood between this ancestor in the 10<sup>th</sup> parentation (1024-mother) and myself was again found to pass through SUZANNA WEVERINGH, and moreover to join the line of descent from JUSTUS VAN DEN BOOGAERT in the person of his granddaughter ANNA CATHARINA DE MOOR. This is seen from the following pedigree:

CLARA CLAESDOCHTER COLIJN and ROMBOUT JACOBZ.

CATHARINA JACOBZ. and ROCHUS VAN CAPELLE.

CLARA VAN CAPELLE and BERNARD I DE MOOR.

BERNARD II DE MOOR and ANNA CATHARINA VAN DEN BOOGAERT.

ANNA CATHARINA DE MOOR and JAN VAN ROYEN.

Just as in the previous case, I have at my disposal the portraits of all these persons, with only one exception: CATHARINA JACOBZ., and so I have been able to convince myself, that none of them (with the exception of ANNA CATHARINA VAN DEN BOOGAERT) showed any special similarity with the person at the top (CLARA COLIJN), whom according to the impartial evidence of many independent judges, I resemble in features, though she shares her contribution to my procreation with 1023 others.

At first sight this observation might seem to stand in contradiction to the theory of saltatory repetition of family-type, as it might be thought illogical to suppose that SUZANNA WEVERINGH did inherit her type at the same time along the line of descent from JUSTUS VAN DEN BOOGAERT and along that from CLARA COLIJN. But a moment's reflection teaches us, that such a double or even multiple derivation of the same hereditary features is by no means impossible or improbable, but on the contrary will occur pretty often.

Why indeed should it be necessary to suppose that the family-type in question started with JUSTUS VAN DEN BOOGAERT in the seventeenth century? Is it not much more probable, that the same repetition of type, which, judging from the portraits occurred twice in the lapse of time from 1623 to 1760, had manifested itself an unlimited number of times in foregoing periods, each time skipping an indefinite number of generations? Nor is it in the least probable that in each case this reappearance of type remained restricted to one single person, and that all these manifestations of the type should be concentrated in the line running through JUSTUS VAN DEN BOOGAERT — SUZANNA WEVERINGH. On the contrary, it seems much



more likely that this type repeatedly became manifest in a number of different but interrelated families, living in the same town or at least in the same neighbourhood. This opinion agrees well with the fact that CLARA COLIJN and her husband ROMBOUT JACOBSZ., as well as GILLES VAN DEN BOOGAERT and his wife CORNELIA VERSPREET, were inhabitants of Antwerp, and belonged to the prosperous merchant-guild, the same being the case with the family DE MOOR. All these families, and many others, that were interrelated with them and with each other, emigrated to Holland in consequence of the troubles and persecutions in the days of the insurrection against Spain.

Undoubtedly they may have imported a certain number of family-types, which they carried in their hereditary material. May be ANNA CATHARINA DE MOOR had obtained a double dose of one of these types, along the lines of both her parents: viz. the type that had become manifest both in her grandfather JUSTUS VAN DEN BOOGAERT and in her great-great-grandmother CLARA COLIJN. It remains to be explained why notwithstanding this double inheritance, the type in question did not once more become manifest before the third generation in descent from ANNA C. DE MOOR, namely in SUZANNA WEVERINGH.

As the starting-point for our consideration we can best refer to the condition at the end of the sixteenth century, which we may imagine to have consisted of a rather large circle of interrelated families, that for centuries continually intermarried, but from time to time begat individual members, who carried the family-types to other Flemish and Dutch towns and even to foreign countries. At the said period this hereditary disposition probably was already rather complicated, but by no means reached the complexity, that arose during the seventeenth century, when numerous Flemish, Brabantic, Walonic and French exiles gradually mixed up with the autochthonic inhabitants to the North of the Rhine-delta.

Now supposing this hypothesis about the saltatory repetition of family-types to be well-founded, it necessarily follows that this type should reappear periodically and therefore also contemporaneously in different persons, whose mutual forefathers rank so high up in their pedigrees, that these bearers of the same type are themselves quite unaware of the existence of blood-relation between them, and consequently consider this similarity as an inexplicable and accidental trick of pure chance.

In short: by the saltatory repetition of family-type a natural explanation might be given of the mysterious but undeniable fact of the "second-self".



A priori there seems to be no plausible reason to consider the occurrence of the second-self as an isolated and independent phenomenon, in need of a special explanation. For the similarity, that so often shows itself between members of the older and younger generations of the same family, cannot reasonably be supposed to be of another character than that which sometimes is seen to exist between two or more descendents of the same remote ancestor. Yet this distinction is very readily made by the greater majority of people. When a person shows a striking likeness to a male ancestor, say e.g. that one of his great-grandfathers, with whom he shares the family-name, nobody will hesitate a moment to ascribe that similarity to blood-relationship. But when the same kind of similarity shows itself between two descendents of that same great-grandfather, who can therefore be relatives in the 9<sup>th</sup> degree, and may differ not only in family-name, but also in all sorts of other features, even in nationality, and be quite unaware of the existence of any blood-relation between them, this phenomenon awakes sensations of astonishment and even awe, and is ascribed to the influence of accident, which only means that no reasonable explanation is deemed possible.

Though therefore the theoretical explanation of the phenomenon of "second-self" as a consequence of blood-relationship seems clear and simple, yet the reconstruction of the concrete proof in each single case of similarity between apparently quite unrelated persons is of course studded with difficulties. In the first place the overwhelming majority of people are completely unacquainted with their higher ancestry; often they do not even know the family-name of their maternal grandmother. So when we want to compare the pedigrees of two persons, who do not appear to be in any way related, we are met with the difficulty that the chances are very much against our obtaining on two lines of descent the evidence of mutual ancestral relationships. But even when we succeed in discovering one or more mutual ancestors, there is no need whatever to suppose, that the type in common should exactly be derived from this ancestor, and as long as we do not discover a portrait of him, the solution of this question will remain impossible. Even if the portrait should really be found, the chance exists, that the common forefather shows features different from those of his descendents, and yet has handed down to them their family-type, which he carried hidden among many others in his genotypical predisposition.

On the other hand we may safely assume, that as soon as it proves possible to trace the pedigrees of a set of two (or more)

persons that show a striking similarity, (say e.g. up till the tenth generation), we will in most cases undoubtedly meet with forefathers in common. This can be expressed shortly by the assertion: All men are blood-relations, in every kind of degree and in many different manners. The relation may be of a very simple character, but also of the highest complication. As it cannot be told beforehand, what will prove the case in each special instance, it seems fairly hopeless to undertake such an investigation concerning the pedigrees of two or more second-selves, and still more to try to collect as many portraits as possible of their ancestors. Even for one single pedigree the search for family-portraits is next to impossible, at least for the private student. I am therefore fully convinced, that the only way to extract any scientific results about the heredity of family-types from what is left us of the likenesses of our forefathers, will be to get them all photographed, and so make them accessible for comparative investigation. As this material is scattered over the whole civilized world, and for the greater part is not provided with the names of the persons represented, it seems very doubtful that such a collection of the iconographic material of Europa and America could ever be brought together. But assuredly mere codification, without reproduction by photography, could only be of very slight use for the study of family-likeness by means of portraits.

Yet the private investigator need not remain inactive, as he can try to apply his hypothesis to a few well-defined cases. For this endeavour he may find encouragement in the consideration, that the above-mentioned check to the discovery of the common forefather of the family-type, hopeless as it may apparently look, can be seen really to contain a strong support for it. Should namely the supposition that an unlimited number of family-types independent of one another, may be hidden in the hereditary material of each person, prove true, then the demonstration of the probability of the above-named hypothesis is considerably simplified. It may be restricted to an elucidation of the question at issue:

Do those ancestors that, according to existing portraits, have strongly influenced the type of one member of a set of closely-resembling persons, also occur in the pedigree of the other member?

I consider that I am able to produce evidence concerning this restricted deduction in a case of resemblance between three gentlemen, which I noticed at a moment, when I was still quite unaware of their mutual relationship. It was in the library of the Dutch Society for Genealogy and Heraldry, called „De Nederlandsche Leeuw”, that I first got sight of the portrait of the well-known

Dutch genealogist Mr. W. J. Baron d'ABLAING VAN GIESSENBERG. The portrait immediately reminded me of my uncle Mr. P. van BEMMELLEN, but at the same time vividly impressed me by its likeness to the late statesman Jhr. Mr. A. F. DE SAVORNIN LOHMAN. These gentlemen were contemporaries, and as the latter two belonged to families, whose pedigrees might probably be investigated with good chance of success, I resolved to make an attempt. Yet, as a matter of fact, such an effort can never lead to a complete pedigree, even when the number of generations is restricted to ten. And even with this restriction we can safely predict, that in any case a certain number of ancestral quarterings in common to both families will be found. To go up still higher than the 10<sup>th</sup> generation will of course only prove possible for a very few families, mostly belonging to royalty or the higher nobility, but in those exceptional cases we may be perfectly assured that we shall find alliances in common. That this is inevitable may be understood by the following consideration:

Mankind of to-day is the product of foregoing generations. Theoretically the number of ancestors of each individual increases at the rate of multiples of two, which in a period of ten centuries, corresponding to thirty generations, leads to a theoretical number of  $2^{30}$  forefathers and -mothers. Such a number will probably already surpass the number of men, capable of existence in those days over the entire habitable surface of the earth, but in any case it greatly exceeds the number of inhabitants of western Europe, that lived there about the year 900, and practically form the ancestors of our nation. This becomes the more stringent, when we take into consideration that only a certain part of the population in those days as well as in others can have contributed to the procreation of posterity, a great number remaining excluded from propagation, by all kinds of reasons: untimely death, illness, coelibacy, sterility etc. So the number of people fit for begetting issue must have been so restricted, that practically all of them must have participated in the procreation of every separate member of the present generation of Europe and America. In other words: every man of the generation of Anno 900, who got children, is the forefather of every white man of to-day.

That this assertion is true, can of course never be proved rigorously and only made probable for a few historical figures of those remote days, e.g. Charles the Great (Charlemagne), but we may safely infer, that it may as well be applicable to all his contemporaries.

In itself the possession of common ancestors therefore implies nothing strange, on the contrary, I have been rather astonished, that



in the case of DE SAVORNIN LOHMAN their number came out to be so low, not only in connection with VAN BEMMELN, but as well, and even more so with D'ABLAING VAN GIESSENBURG. Notwithstanding that, I succeeded in tracing a few quarterings in common to all three, and in one case to ascend to a mutual forefather. I was greatly surprised and pleased to find, that a few of these quarterings led to the same circle of families at Antwerp, which I mentioned before, and in the case of D'ABLAING VAN GIESSENBURG even to the family JACOBSZ., to which belonged the husband of CLARA COLIJN.

Though I did not succeed in finding either the name COLIJN, or that of VAN DEN BOOGAERT, among the ancestors of both D'ABLAING VAN GIESSENBURG and DE SAVORNIN LOHMAN, I don't think that this must be considered as a serious obstacle against my hypothesis. For we must never forget, that JUSTUS VAN DEN BOOGAERT may as well have obtained his face and complexion from his mother CORNELIA VERSPREET, as from his father GILLES, and that the mother of this CORNELIA, also named CORNELIA, was a daughter of the family BRUYNSEELS, that probably stood in blood-relationship along many different lines with the remaining merchant-families of Antwerp, mentioned in this paper.

When we look at the question from this point of view, we clearly conceive how unscientific it would be only to attach value to a name. Yet names are the last thing left, in tracing family-relations, when all other indications fail, and so it is clear that exact genealogical studies must form the foundation of every investigation of family-resemblance.

It need not be specially mentioned, that we should not restrict ourselves to the external features, but may and even must extend these investigations to all bodily and mental characters, and so try to make as complete a reconstruction of our ancestors as possible. Especially on the latter field we can often still obtain important results, even when all indications about the material personality fail. By the study of his mental inheritance in publications and letters, and even by the graphological analysis of his manuscripts, as well as by the knowledge of his rôle in public and private life, we may obtain a good insight into the character and the remaining mental disposition of many a forefather, or, when not of himself, at least of his nearest bloodrelations. When we take into consideration, that undoubtedly in many cases an intimate connection exists between bodily and mental features, we may be led to more or less probable conceptions about the former by the study of the latter. From this point of view it may prove of interest, that Mr. P. VAN BEMMELN,



who undoubtedly had inherited his external features from his grandmother SUZANNA WEVERINGH, had probably obtained his juristic predisposition not only from her side, but as well from his grandfather PIETER PAMA DE KEMPENAER. He shared this legal ability with his uncle Mr. JACOBUS MATTHEUS DE KEMPENAER. In this respect it is assuredly remarkable, that also his second-selves, Mr. D'ABLAING VAN GIESSENBURG and Mr. DE SAVORNIN LOHMAN, have distinguished themselves in the realms of the law.

The two brothers of P. VAN BEMMELEN, JACOB MAARTEN SR. and ADRIAAN ANTHONY, did not possess such a striking similarity to SUZANNA WEVERINGH, and showed no juristic disposition, but were naturalists. But by the issue of the former of these two, it becomes at least probable that also JACOB MAARTEN VAN BEMMELEN SR. carried in his hereditary material not only the facial type of his maternal grandmother, but also the juridical predisposition of both his maternal grandparents. Taking this aspect of the question, it might prove of interest, that the pedigrees of these three personalities: D'ABLAING VAN GIESSENBURG, DE SAVORNIN LOHMAN and VAN BEMMELEN, have led me to an ancestor common to all three of them: AEM VAN DER BURCH, a member of the well-known municipal family of Delft, now extinct (according to the popular conception of this word). This man lived about 1400, and had a daughter BAERTE, who married GERRIT GERRITSZ. BENNINGH, the founder of the well-known patrician family BENNINGH or BANNING of Amsterdam. This alliance led to the families D'ABLAING and VAN BEMMELEN, in both cases along two different paths.

Furthermore he had a son HENDRIK, who married AEGHT HART VAN DER WOERT and had a daughter HADEWICH, who married twice, first with WILLEM ALBRECHTSZ. PIJNSSEN VAN DER AA, which union led to ancestors of Mr. D'ABLAING VAN GIESSENBURG and Mr. DE SAVORNIN LOHMAN, and a second time with REYER DIRCKSZ. VAN HEEMSKERCK, which made her a female ancestor of the issue of the couple DE KEMPENAER-WEVERINGH, on both paternal and maternal lines of descent.

But still further we find that out of the second marriage of HADEWICH VAN DER BURCH there issued a grand-daughter called ELSJE VAN HEEMSKERCK, who, by marrying HUYG CORNELISZOOM DE GROOT, became the grandmother (on the fathers' side) of the famous HUGO DE GROOT. So perhaps it might be suggested, that the accurate investigation of the complete progeny of AEM VAN DER BURCH could furnish us with arguments, that proportionately it contained a greater number of members with juridical predisposition than other similar families, accessible for statistical supervision. The number of these

descendents must needs amount to several thousands, and the investigation therefore will prove exceedingly laborious and difficult, but on the other hand it is fairly certain, that only by the comparison of very large numbers of persons in a long series of generations it will be possible to exclude the influence of numerous external circumstances (such as habit, tradition, social and religious tendencies) which have no direct connection with heredity.

*Groningen* September 1924.

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**Palaeontology.** — “*Neotenie, Persistenz, Degeneration.*” Von Dr. A. KIESLINGER, Wien. (Communicated by Prof. H. A. BROUWER).

(Communicated at the meeting of November 29, 1924).

Die einzelnen Merkmale eines Organismus stehen in Bezug auf ihre Organisationshöhe in einem gewissen Zusammenhange (Korrelation). Man hat daher in vielen Fällen geglaubt, aus der Entwicklungsstufe eines Organes auf den Rang der ganzen Form (“primitiv, differenziert”) schliessen zu können. Es stellte sich heraus, dass dies nicht ganz richtig sei, dass strenggenommen jedes Organ seine eigene Wachstumsgeschwindigkeit besässe (“Heterochronie” der Organe), welche allerdings für bestimmte engere Gruppen bleibend und bezeichnend ist. Aber auch hier ergaben sich Unterschiede durch früheres oder späteres Eintreten des einen oder andern Merkmals. Je nach dem Standpunkt des Beschauers wurden diese Abweichungen vom Gewöhnlichen als Beschleunigung oder Hemmung des Wachstums aufgefasst. Der eine Vorgang wurde von GIARD als Progenese (3), der andere von KOLLMANN als Neotenie (1) bezeichnet. Spätere Autoren haben beide Vorgänge, die doch ihrer ursprünglichen Begriffsfassung nach Gegensätze bedeuteten, für gleich erachtet. In verschieden weiter Fassung geht besonders der erste Begriff durch das zoologische Schrifttum.

KOLLMANN ging von der Erscheinung aus, dass bei manchen Anuren und Urodelen die Verwandlung zum richtigen Zeitpunkte unterbleibt. Die Larven überwintern, werden grösser als gewöhnlich und können unter Umständen (manche Urodelen, bes. auffällig beim mexikanischen Axolotl, *Amblystoma tigrinum*) sogar geschlechtsreif werden, ohne die völlige Entwicklung erreicht zu haben. Dies nannte KOLLMANN Neotenie (partielle: das längere Beibehalten jugendlicher Merkmale, vollständige: das Andauern dieser Merkmale bis über die Zeit der Geschlechtsreife hinaus). Fragen wir hier nach der relativen und absoluten Stellung der Teilvorgänge, so ist das Normale hier das Eintreten der Geschlechtsreife zum normalen Zeitpunkt, das Abnormale liegt im Ausbleiben der Umwandlung, im Beibehalten der jugendlichen Merkmale bis in eine Zeit hinein, wo das Tier, an andern seiner Art gemessen, durchaus nicht mehr jung ist. Es liegt also eine wirkliche (nicht bloss relative) Verzögerung in

der Entwicklung ganzer Organgruppen vor. Wenn nur ein einzelnes Organ zurück bleibt, wäre besser von Epistase (EIMER) zu sprechen. Wir fassen zusammen: Neotenie hat dann statt, wenn bei sonst normal fortschreitendem Wachstum eine Organgruppe dauernd oder auf längere Zeit zurückbleibt, wenn ein in vieler Hinsicht erwachsenes Tier infantile Merkmale aufweist. Das Gegenteil, Progenese, hat statt, wenn bei sonst normalem Wachstum und normaler Entwicklung eine Organgruppe in Entwicklung und Funktion den übrigen vorausschneit. So haben GIARD und BONNIER (4) beide Vorgänge unterschieden<sup>1)</sup> und es ist bedauerlich, dass in der Folgezeit diese Begriffstrennung wieder verwischt wurde<sup>2)</sup>.

J. E. V. BOAS hat 1896 den Erscheinungen der Neotenie eine eigene Arbeit gewidmet (5) und dabei auf die weite Verbreitung derartiger Erscheinungen im ganzen Tierreiche überhaupt hingewiesen. Den besonderen Wert dieser Erkenntnis sah er darin, dass dadurch viele Merkmale, die bisher als "primitiv" galten und sich schlecht in die sonstige systematische Stellung ihres Trägers einpassten, nunmehr mit Hilfe des Neotenie-Begriffes zwanglos erklärt werden konnten.

BOAS ist vielleicht in manchem zu weit gegangen. Er legt wenig Wert auf die Unterscheidung von Neotenie und Progenese<sup>3)</sup>, zählt dagegen auch das Zurückbleiben einzelner Organe (doppelte Vagina bei einzelnen placentalen Säugern, Zurückbleiben einzelner Knorpel im Vorgang der Verknöcherung usw.) zu den Belegen für Neotenie, was wohl nicht dem ursprünglichen Begriffsumfang entspricht.

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<sup>1)</sup> G. und B. bringen folgende Beispiele (zitiert nach BOAS): Ein Fall von teilweiser Neotenie liegt z. B. vor, wenn ein erwachsener Mensch das Milchgebiss beibehält, ein Fall von Progenese, wenn das Funktionieren der Geschlechtsorgane schon bei einem Kinde eintritt. Den ersten der beiden Fälle würden wir heute wohl als Epistase bezeichnen.

<sup>2)</sup> Vgl. u. a. die Erklärung von Neotenie und Progenese in „Kultur der Gegenwart“ IV/1, Allgemeine Biologie 1915, S. 428 f. (E. GODLEWSKI).

<sup>3)</sup> Wenn B. am Ende seiner Arbeit (a. a. O.) sagt: „Sämtliche hier angeführte Fälle von Neotenie haben das Gemeinsame, dass das Tier auf einer Entwicklungsstufe geschlechtsreif wird, auf welcher seine übrigen Organe — alle oder einige — nicht die volle Ausbildung erreicht haben und dann überhaupt diese Ausbildung nicht erreichen. Manchmal findet aber eine vorzeitige Reife der Geschlechtsorgane, resp. eine verspätete Ausbildung gewisser anderer Organe statt, ohne dass Neotenie daraus resultiert...“, so ist das auf Umwegen eine unfreiwillige Anerkennung der „Progenese“ GIARDS.

Die Beschränkung des Begriffes Neotenie auf solche Formen, welche die völlige Ausbildung überhaupt nicht erlangen, möchte ich als unwesentlich ablehnen. Sagt doch z. B. KOLLMANN vom Axolotl (2, S. 268), er könne „Jahre hindurch oder sein ganzes Leben auf der Perennibranchiatenform stehen bleiben.“



Derartige Einzelercheinungen werden heute meist als Hemmungsbildung oder Epistase (EIMER) bezeichnet und "Neotenie" auf das Zurückbleiben ganzer grosser Organgruppen, welche den allgemeinen Habitus des Tieres bedingen, beschränkt. Der Unterschied zwischen Neotenie und Epistase ist also im wesentlichen ein gradueller. So hat es wohl auch KOLLMANN gemeint, wenn er vom Axolotl sagt (1, S. 393): "... das Wort "Hemmungsbildung" ist hier nicht am rechten Platz, weil dieser Begriff gleichzeitig den eines pathologischen Eingriffes und den Hinweis der Lokalisierung auf einzelne Organe in sich schliesst".

Es hat einen gewissen Reiz, den Erscheinungen der Neotenie, welche in der lebendigen Tierwelt eine so grosse Rolle spielen, auch in der fossilen nachzuspüren und zwar sollen fossile Cephalopoden als Beispiel herangezogen werden.

H. SCHMIDT (Göttingen) hat Studien über Neotenie bei Goniatiten angestellt, über die er auf der Tagung der Paläontologischen Gesellschaft zu Eichstädt 1924 berichtet hat. Leider liegt diese Arbeit noch nicht im Druck vor, so dass hier nicht auf Einzelheiten eingegangen werden kann. SCHMIDT geht, wenn ich ihn recht verstanden habe, von einigen globosen Goniatitentypen aus. Diese kugeligen Jugendformen entwickeln sich einerseits zu solchen, welche die plumpe Gestalt beibehalten, anderseits zu andern, welche den Querschnitt ändern und flach werden. (Es liegen hier also „Divergenzformen" vor, wie ich dies seinerzeit [8, Nachtrag S. 140] genannt habe). Diejenigen Gehäuseformen nun, welche ihren runden Querschnitt beibehalten, hält SCHMIDT für neotenisch.

Was an SCHMIDTS Untersuchung vor allem auffällt, ist die geringe Bewertung der Lobenlinie, welche für ihn durch die Gehäuseform bedingt und daher ganz nebensächlich erscheint. Weit entfernt, das Ziel der Ammonitenforschung in einer unermüdlichen Graphologie der Loben zu suchen, möchte ich hier doch eine Apologie dieser missachteten Linien wagen. Es kann nicht scharf genug betont werden: Die Lobenlinie steht in nur sehr losem Zusammenhang mit der stereometrischen Gehäuseform. Ueberaus gross ist die Zahl der Konvergenzformen, grösser als die der alleinstehenden, nicht nur unter Ammoniten, sondern auch zwischen Ammoniten und Nautiliden. Zahlreiche Gehäuse gleichen einander in Form, Skulptur und Zuwachsstreifen so vollkommen, dass erst die auspräparierte Lobenlinie ihre wahre Natur enthüllt. Wenn irgend ein Teil des Ammonitengehäuses, so sind es die Kammerscheidewände, welche Rückschlüsse auf die Weichteile zulassen. Die Aussenschalen sind in ihrer Gestalt ein Kompromiss aus Umwelt und Eigenleben, sie umfassen einen geringen Formenschatz, der schon im Perm im Wesentlichen erschöpft ist und sich in der Folgezeit oftmals wiederholt. Was wüssten wir von allen Familien ohne jenes wichtigste Merkmal? Was wüssten wir überhaupt von den Ammoniten?

Zur globosen Körperform: Warum soll sie für Jugendformen allein charakteristisch, bei alten daher neotenisch sein? Ist der „*Arcestes*-Typus" nicht wahrscheinlicher das Ergebnis einer bestimmten Lebensweise, über die wir allerdings nichts wissen? Ich halte also in dem Goniatitenbeispiel den Schluss auf Neotenie für durchaus

nicht zwingend und will im Folgenden versuchen, einen solchen auf der Lobenlinie, die ich für ebenso bedeutend halte wie SCHMIDT die Gehäuseform, aufzubauen.

Die vorliegende Untersuchung basiert auf dem schönen Triasmaterial, das von der 2. Niederländischen Timorexpedition aufgesammelt wurde und von dem ich einen kleinen Teil bearbeitet habe (8 und 9).

Unter den Nautiliden der Triasformation spielt die Gattung *Proclydonautilus* eine Hauptrolle. Es sind meist scheibenförmige



Fig. 1. *Proclydonautilus singularis* WELTER. Gekammerter Steinkern in  $\frac{2}{3}$  der nat. Grösse, Timor (Nifokoko). Obertriadische Hallstätter Kalke. Vereinfacht aus WELTER, a. a. O. Taf. XXXII, Fig. 7 und 14. Original in Delft.

Gehäuse mit weitgehender Einrollung (also engem Nabel) und einer für einen Nautilus sehr stark bewegten Suture. (Bezeichnende

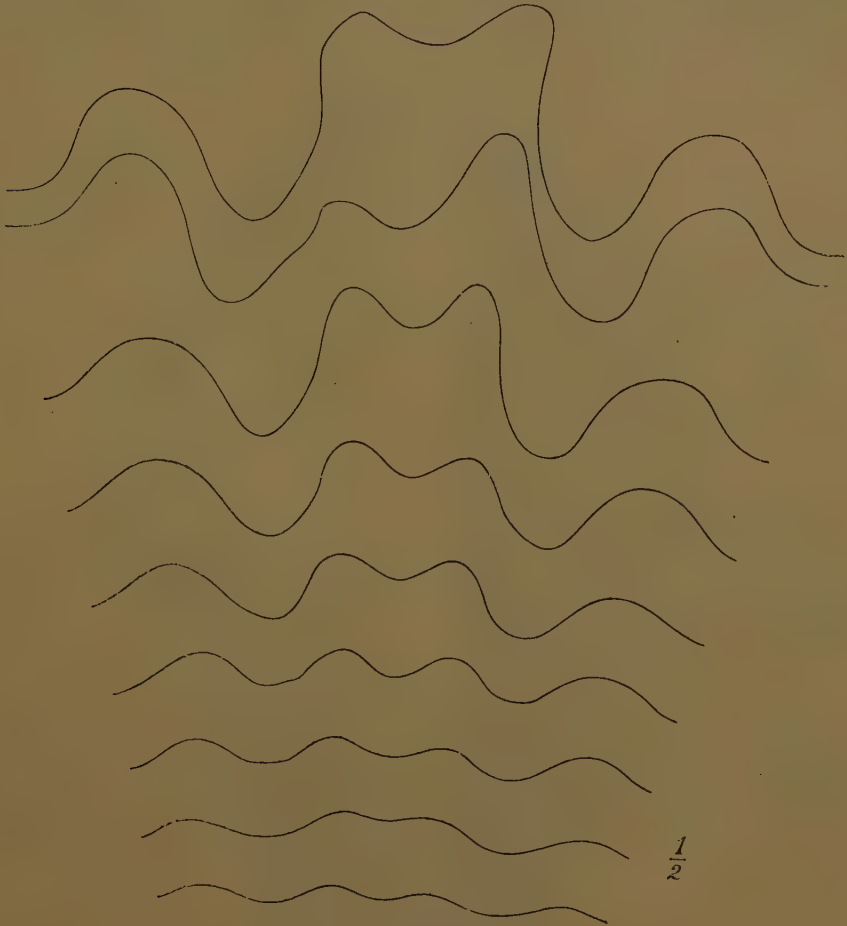


Fig. 2.

Abgewinkelte Lobenlinie von *Proclydonautilus singularis* WELTER in  $\frac{1}{2}$  natürlicher Grösse. Die Entwicklung vom einfachen *Paranautilus*-Stadium zur *Proclydonautilus*-Suture ist deutlich zu sehen. Die Loben rechts u. links nicht ganz symmetrisch (Aus WELTER, a. a. O., Textfig. 82).

Formen in Fig. 6 u. 7). Die Jugendformen beginnen aber mit einfachen geraden Linien ("*Paranautilus*-Stadium"). Wiederholter Wechsel des Querschnitts, gelegentlich leichte Skulpturen ("*Cosmonautilus*") ermöglichen es, verschiedene "Arten" zu unterscheiden. Ich habe an anderer Stelle (8, Nachtrag) die innige biologische Verknüpfung dieser Formen aufgezeigt, die eine so scharfe Artentrennung, wie sie dem Paläontologen erwünscht wäre, unmöglich macht. Der enge Zusammenhang der einzelnen "Arten" von *Proclydonautilus* ist hier für uns von besonderer Bedeutung, denn er berechtigt uns, für diese Formen,

die alle sehr ähnlich sind und die gleiche Grösse erreichen, ein ungefähr gleichschnelles und gleichmässiges Wachstum anzunehmen. Dies ist eine der Grundlagen für das Folgende.

Im Jahre 1914 hat nun WELTER eine sonderbare neue Form unter



Fig. 3.

Jugendform eines grossen *Proclydonautilus singularis* WELTER aus Timor. Zu beachten die einfachen Loben.  $\frac{1}{2}$  natürlicher Grösse. Nach KIESLINGER.

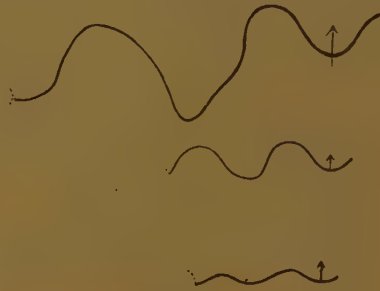


Fig. 4.

Drei Lobenlinien des Stückes von Fig. 3.  $\frac{1}{2}$  natürlicher Grösse. Nach KIESLINGER.

dem Namen *Proclydonautilus singularis* aus Timor beschrieben (7, S. 211, Textf. 82, Taf. XXXII, Fig. 7 und 14). Fig. 1 und 2 sollen eine beiläufige Vorstellung geben. Im Jahre 1922 konnte ich auf Grund der Aufsammlungen der zweiten Timorexpedition die

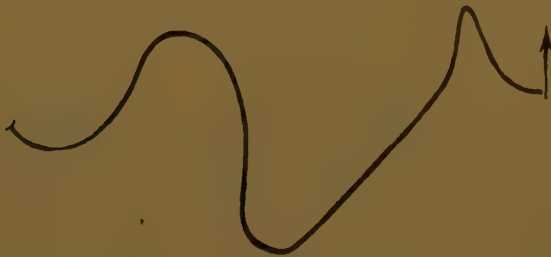


Fig. 5.

Reife Lobenlinie von *Proclydonautilus singularis* WELTER in  $\frac{1}{2}$  natürlicher Grösse. Nach KIESLINGER.

Beschreibung WELTERS wesentlich ergänzen (8). Die neue Art ist schon durch ihre Querschnittsverhältnisse leidlich gut von ihren Nachbarn getrennt; was sie aber besonders auszeichnet, ist der Umstand, das die jugendliche "*Paranautilus*-Sutur" nicht wie bei allen nächsten Verwandten bei einem kleinen Durchmesser (höchstens



3—4 cm) verschwindet, sondern dass sie bis ca. 8 cm Durchmesser, also schon einem ansehnlichen Grössenstadium des Tieres, rein anhält und erst zwischen 9 und 13 cm Durchmesser sich zur reifen *Proclydonautilus*-Sutur umbildet (Fig. 2 bis 5). In Grössenstufen



Fig. 6.

Ausgewachsenes Stück von *P. singularis*.  $\frac{1}{2}$  natürlicher Grösse. Nach KIESLINGER.

also, in denen alle andern Clydonautilen schon eine ausgebildete Sutur haben (Fig. 7), zeigt *P. singularis* noch zweifellos jugendliche Merkmale. Erst viel später holt er das Versäumte ein und wächst normal weiter bis zur durchschnittlichen Höchstgrenze von 25 cm DM. (Fig. 6).

Hat hier vielleicht eine zeitweise Verlangsamung der Gesamt-

entwicklung stattgefunden? Wir haben oben gesehen, dass die innige Verwandtschaft und Durchkreuzung dieser Formen eine solche Annahme unwahrscheinlich macht. Viel deutlicher aber sprechen die regelmässige zunehmenden Abstände der Loben, von



Fig. 7.

Lobenlinie von *Proclydonautilus Goniatites* HAUER in natürlicher Grösse. Man beachte die tiefen Loben trotz der geringen Grösse im Vergleich zu Fig. 2 und 3. Diese nur in halber Grösse! Nach KIESLINGER.

denen keiner aus der arithmetischen Reihe herausfällt. Eine Verzögerung des Wachstums und ein nachfolgendes rascheres Einholen des Versäumten (wie dies WELTER andeutet) liesse sich damit nicht vereinigen. Nun ist die Kammerscheidewand sicher einer der wenigen Teile des Cephalopodengehäuses, die mit der inneren Organisation, mit den Weichteilen in engem Zusammenhang stehen und Rückschlüsse auf dieselben zulassen. Wir haben somit bei sonst normaler Entwicklung ein auffallend langes Zurückbleiben der Lobenlinie und mit ihr sicher eines grossen Teiles der inneren Organe auf einem niederen Entwicklungsgrad, somit einen typischen Fall von Neotenie vor uns.

Vollständige (totale) oder teilweise (partielle) Neotenie im Sinne KOLLMANN'S (1, S. 394)?

WILLEY sagt (11, S. 746) über den rezenten *Nautilus* auf Grund eingehender Studien am lebenden Tier: „It has been suggested, and I think in some quarters adopted as a dogma, that the formation and succession of septa (in *Nautilus*) is correlated with the recurrence of reproduction periods. This is not the case, since, according to my observations, propagation only takes place after the last septum is formed” und (S. 747) ”The progressive growth of the animal is accompanied by the addition of new chambers, which

give increased buoyancy and so maintain the shell under the entire control of the animal until a limit is reached when the last air-chamber has been divided off, and then only does propagation commence". Also erst nach Vollendung des ganzen Gehäuses wird der Nautilus geschlechtsreif (und stirbt wahrscheinlich bald darauf). Mit einer gewissen Berechtigung dürfen wir dasselbe für die fossilen Nautilen annehmen und haben daher einen Fall einer teilweisen Neotenie vor uns.

Dadurch, dass die hier beschriebene Erscheinung nicht auf einzelne Individuen beschränkt, sondern allem Anschein nach für eine „Art“ bezeichnend ist, fällt sie gleichzeitig unter EIMERS Begriff der Genepistase. Darunter verstand EIMER eine Artentrennung, hervorgerufen durch „das Stehenbleiben einer Anzahl von Individuen auf einer bestimmten Stufe der Entwicklungsreihe, während die übrigen in der Umbildung weiterschreiten“ (10, S. 34).

Es ist verlockend, die Linien weiter zu verfolgen. Seit dem Perm haben wir neben anderen einfache, indifferente Gehäusetyphen, die über das *Paranautilus*stadium überhaupt nicht hinausgehen. Während im Perm die Gruppe der „*Nautili simplices*“, in der Trias die Gattung *Paranautilus* eine geringe Rolle spielen, sind diese „einfachen“ Formen vom Lias an herrschend. Gelegentlich haben sie Ableger mit einer stärker differenzierten Lobenlinie (z.B. *Aturia*). Im Grossen und Ganzen aber bleibt es dabei. Die Schale scheint primitiv. Das Tier ist es sicher nicht, wie wir aus der Anatomie des rezenten Nautilus wissen. Ob wir es nicht mit einem Falle von Neotenie von einer grossartigen zeitlichen Erstreckung (also Genepistase im Sinne von EIMER) zu tun haben? Mit einer von jenen Formen, wie solche BOAS beschrieben hat, welche auf so sonderbare Weise primitive Merkmale in einem sonst hochentwickelten Gesamttypus enthalten? Besteht zwischen Neotenie und Persistenz ein Zusammenhang?

Zwei Arbeiten kommen dieser Problemstellung nahe: WILLEY hält den rezenten Nautilus (11, S. 810) für das Endglied einer Entwicklung und verallgemeinert: „Fixity of type is the expression of a completed evolution, and this is meant when a particular type is said to be highly specialised in a given direction. *Fixed types are very likely the same as persistent types*, and they have some properties in common amongst which are their limited range of variation and their defective power of regeneration“. Das letzte Argument muss für unseren Fall sofort ausscheiden, weil die Regenerationsfähigkeit an Fossilien nicht nachweisbar ist. Dass persistente Typen

immer extrem spezialisierte seien, dürfte mit den bisherigen Erfahrungen schlecht zusammenstimmen. Gerade indifferente Typen (etwa *Lingula*) sind persistent, gerade extrem spezialisierte sterben rasch aus. So hoch organisiert der rezente *Nautilus* ist, so fehlt jeder Hinweis, dass er sich nicht nach irgend einer Richtung weiterbilden könne. Wiederholt im Mesozoikum und noch im Tertiär hat sich vom Stamme des einfachen "*Nautilus sensu stricto*" eine "*Aturia*-form" losgelöst. Warum soll dies in Zukunft unmöglich sein?

Wenn also auch die hohe Entwicklungsstufe des *Nautilus* zugegeben wird, so kann sie doch nicht als Endpunkt ("completed evolution") aufgefasst werden und ebensowenig dürfen die Begriffe "persistent" und "extrem spezialisiert" für kausal verbunden gehalten werden.

Die zweite Arbeit stammt von J. P. SMITH. Er hat eine überaus sorgfältige Untersuchung über die Auswirkung des "biogenetischen Grundgesetzes" bei Ammoniten angestellt und an der Ontogenie vieler Formen die Unterdrückung und Ineinanderschachtelung ("telescoping" GRABAU) vieler Stadien exakt nachgewiesen (6). Als Gegensatz zu dieser "acceleration of development" ("Tachygenesis" HYATT) führt er mehrere Vorgänge einer "retardation" an, die zu Entartung führen. Darunter gibt es auch ein "stretching the ontogeny": "as when a specialised group remains longer in the larval and adolescent stages than did its ancestors, while finally reaching to the full perfection that they had attained". Also Neotenie. Schon das Stehenbleiben auf einer gewissen Organisationshöhe ("cessation of progress") ist für SMITH "the first step towards degeneration" und führt zunächst zu "fixed types", denen der weitere Verfall folgt. Dies stimmt gut mit den verschiedenen Experimenten, bei denen man Neotenie künstlich hervorgerufen hat, meist durch Unterernährung der Versuchstiere (BOAS, CHAUVIN, etc.).

Wir sehen also Neotenie in Verbindung mit zwei anscheinend gegensätzlichen Vorgängen, nämlich mit Persistenz und Degeneration. Vielleicht können spätere Ergebnisse den Widerspruch aufklären.

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**Mathematics.** — "*The equivalence in  $R_n$  of the  $n$ -dimensional simplex star and the spherical neighbourhood.*" By WILFRID WILSON.  
(Communicated by Prof. L. E. J. BROUWER.)

(Communicated at the meeting of December 27, 1924).

The object of this paper is to prove the theorems I and II stated beneath. So far as the writer is aware these theorems have not yet been explicitly stated and proved, but have been implicitly used in several topological investigations. Some related theorems are stated and proved by H. KNESER in a paper in these Proceedings, the proof sheets of which I have seen through the intermediation of Prof. BROUWER.<sup>1)</sup>

### *The Simplex star.*

In the  $m$ -dimensional number space  $R_m$  consider a finite number of  $n$ -dimensional simplexes, ( $n \leq m$ ) of common vertex  $A_0$  and such that:

(a). Any  $(n-1)$ -dimensional face of vertex  $A_0$  is common to two and only two  $n$ -dimensional simplexes;

(b). Any two  $n$ -dimensional simplexes have in common either (1) no point other than  $A_0$ , or (2) one  $p$ -dimensional face and all its  $(p-k)$ -dimensional faces, ( $p \leq n-1$ ;  $k=1, 2, \dots, p$ ).

The set of points constituting these simplexes and their boundaries is called an  $n$ -dimensional simplex star of centre  $A_0$ ; those  $(n-p)$ -dimensional faces, ( $p=1, 2, \dots, n$ ), of which  $A_0$  is not a vertex are called the boundary of the star while the remaining points are called the interior.

### *Regular subdivision of a simplex star.<sup>2)</sup>*

Let  $\alpha_i$  be the number of  $i$ -dimensional simplexes, ( $i=0, 1, \dots, n$ ), of the  $n$ -dimensional star  $S_n$ , so that any simplex of  $S_n$  may be written  $\alpha_j^i$ , ( $i=0, 1, \dots, n$ ;  $j=1, 2, \dots, \alpha_i$ ), the  $\alpha_j^0$ , ( $j=1, 2, \dots, \alpha_0$ ), being the vertices. In the interior of  $\alpha_j^i$  take an arbitrary point  $P_j^i$ ,  $P_j^0$  being the vertex  $\alpha_j^0$ , and subdivide  $S_n$  into a set  $\bar{S}$  of  $n$ -dimensional simplexes, in the following way:

<sup>1)</sup> H. KNESER, "Ein topologischer Zerlegungssatz", § 1, Satz 3 ( $m$ ) and 4 ( $m$ ), these Proceedings 27, p. 603.

<sup>2)</sup> VEULEN, Cambridge Colloquium, Analysis Situs, p. 85—86.

- (0) The vertices of  $\overline{S}$  are the points  $P_j^i$ , ( $i=0, 1, \dots, n; j=1, 2, \dots, a_i$ ).
- (1) The 1-dimensional simplexes of  $\overline{S}$  are the segments which join the point  $P_j^i$  to each vertex of  $\overline{S}$  in the boundary of  $a_j^i$ , ( $i=1, 2, \dots, n; j=1, 2, \dots, a_i$ ).
- $\vdots$
- ( $k$ ) A  $k$ -dimensional simplex of  $\overline{S}$  is the set of points on all segments joining a point  $P_j^i$  to the points of a  $(k-1)$ -dimensional simplex of  $\overline{S}$  in the boundary of  $a_j^i$ , ( $i=k, k+1, \dots, n; j=1, 2, \dots, a_i$ ).
- $\vdots$
- ( $n$ ) An  $n$ -dimensional simplex of  $\overline{S}$  is the set of points on all segments joining a point  $P_j^n$  to the points of an  $(n-1)$ -dimensional simplex of  $\overline{S}$  in the boundary of  $a_j^n$ , ( $j=1, 2, \dots, a_n$ ).

It follows from these definitions that any  $n$ -dimensional simplex of  $\overline{S}$  has the form  $P_q^0 P_r^1 \dots P_s^n$  and that the number of simplexes in  $\overline{S}$  is finite (being  $(n+1)!$  times the number in  $S_n$ ).

**Theorem 1.** Any point  $P$  of the interior of an  $n$ -dimensional star  $S_n$  is the centre of an  $n$ -dimensional star  $S'_n$  composed of simplexes of a regular subdivision  $\overline{S}$  of  $S_n$ .

Let  $P$  be in the  $k$ -dimensional simplex  $a_s^k$  of  $S_n$ , ( $0 \leq k \leq n$ ). Choose the subdivision  $\overline{S}$  so that  $P_s^k = P$ , and let

$$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n = \overline{a}_w^n$$

be any  $n$ -dimensional simplex of  $\overline{S}$  of vertex  $P_s^k$ .

From the definitions (0), (1),  $\dots$ , ( $n$ ) it follows that

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n$  is in the simplex  $a_w^n$  of  $S_n$ ,

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1}$  is in the  $(n-1)$ -dimensional face  $a_v^{n-1}$  of  $a_w^n$ ,

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k$  is in the  $k$ -dimensional face  $a_s^k$  of  $a_v^{n-1}$ ,

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1}$  is in the  $(j+1)$ -dimensional face  $a_r^{j+1}$  of  $a_s^k$ ,

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j$  is in the  $j$ -dimensional face  $a_q^j$  of  $a_r^{j+1}$ ,

$P_l^0 P_m^1 P_n^2 \dots P_p^{j-1}$  is in the  $(j-1)$ -dimensional face  $a_p^{j-1}$  of  $a_q^j$ ,

$P_l^0 P_m^1 P_n^2$  is in the 2-dimensional face  $a_n^2$  of  $a_p^{j-1}$

$P_l^0 P_m^1$  is in the edge  $a_m^1$  of  $a_n^2$  and

$P_l^0$  is the vertex  $a_l^0$  of  $a_m^1$ .

Since  $P_s^k$  is an interior point of  $S_n$ , the  $(n-1)$ -dimensional face  $\alpha_n^{n-1}$  containing it, must have the centre of  $S_n$  as a vertex and therefore by (a) of the definition of a star,  $\alpha_v^{n-1}$  is common to two and only two  $n$ -dimensional simplexes  $\alpha_w^n$  and  $\alpha_{w'}^n$  of  $S_n$ .

By the concluding remark of the previous paragraph the number of the simplexes  $\bar{\alpha}_w^n$  is finite. We require to prove that they satisfy conditions (a) and (b) of the definition of a simplex star.

(a) The  $(n-1)$ -dimensional faces of  $\bar{\alpha}_w^n$  of vertex  $P_s^k$  are

$$(1) P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n$$

$$(2) P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n,$$

( $j = 1, 2, \dots, k-1, k+1, \dots, n-1$ ), and

$$(3) P_l^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1}.$$

(1) Let  $P_l^0$  and  $P_{l'}^0$  be the vertices of  $\alpha_m^1$ . Then:

By definition (1) of Subdivision,  $P_{l'}^0 P_m^1$  is an edge of  $\bar{S}$ , hence by definition (2) of subdivision,  $P_{l'}^0 P_m^1 P_n^2$  is a 2-dimensional simplex of  $\bar{S}$ . Applying definitions (3), (4),  $\dots$ ,  $(n-1)$  and  $(n)$  in succession we prove that  $P_{l'}^0 P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n$  is an  $n$ -dimensional simplex of  $\bar{S}$ . Thus  $P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_s^k \dots P_v^{n-1} P_w^n$  is common to two  $n$ -dimensional simplexes of  $\bar{S}$ . Any other  $n$ -dimensional simplex having the face  $P_m^1 P_n^2 \dots P_w^n$  must be of the form  $P_{l''}^0 P_m^1 \dots P_w^n$  and by definition (1) of the regular subdivision,  $P_l^0 P_m^1$  and  $P_{l'}^0 P_m^1$  are the only edges of  $\bar{S}$  of the form  $P_{l''}^0 P_m^1$  incident with  $P_m^1$ . Therefore  $l''$  must be  $l$  or  $l'$ . Thus

$$P_m^1 P_n^2 \dots P_p^{j-1} P_q^j P_r^{j+1} P_s^k P_v^{n-1} P_w^n$$

is incident with two and only two  $n$ -dimensional simplexes of  $\bar{S}$ .

(2) The  $(j-1)$ -dimensional face  $\alpha_p^{j-1}$  is incident with two  $j$ -dimensional faces  $\alpha_q^j$  and  $\alpha_{q'}^j$  of  $\alpha_r^{j+1}$ . Therefore by definition (j) of regular subdivision there are two  $j$ -dimensional simplexes  $P_l^0 \dots P_p^{j-1} P_q^j$  and  $P_{l'}^0 \dots P_p^{j-1} P_{q'}^j$  of  $\bar{S}$  and by applying successively the definitions (j),  $(j+1)$ ,  $\dots$ ,  $(n)$  of regular subdivision we obtain two simplexes  $P_l^0 \dots P_p^{j-1} P_q^j P_r^{j+1} \dots P_w^n$  and  $P_{l'}^0 \dots P_p^{j-1} P_{q'}^j P_r^{j+1} \dots P_w^n$  of  $\bar{S}$  having  $P_l^0 \dots P_p^{j-1} P_r^{j+1} \dots P_w^n$  as common  $(n-1)$ -dimensional face. Any other  $n$ -dimensional simplex having this face must be of the form:



$P_l^0 \dots P_p^{j-1} P_{q''}^j P_r^{j+1} \dots P_w^n$ , where by definition  $(j+1)$  of regular subdivision  $\alpha_{q''}^j$  is a  $j$ -dimensional face of  $\alpha_r^{j+1}$  incident with  $\alpha_p^{j-1}$ , that is,  $\alpha_{q''}^j$  is either  $\alpha_q^j$  or  $\alpha_{q'}^j$  and thus  $P_{q''}^j$  is either  $P_q^j$  or  $P_{q'}^j$ . Thus  $P_l^0 \dots P_p^{j-1} P_r^{j+1} \dots P_w^n$  is an  $(n-1)$ -dimensional face of two and only two  $n$ -dimensional simplexes of  $\overline{S}$ .

(3) The  $(n-1)$ -dimensional face  $\alpha_v^{n-1}$  being common to two and only two  $n$ -dimensional simplexes  $\alpha_w^n$  and  $\alpha_{w'}^n$  of  $S_n$ , it follows from definition (n) of regular subdivision that the  $(n-1)$ -dimensional face  $P_l^0 P_m^1 \dots P_v^{n-1}$  of  $\overline{S}$  is common to two and only two simplexes  $P_l^0 P_m^1 \dots P_v^{n-1} P_w^n$  and  $P_l^0 P_m^1 \dots P_v^{n-1} P_{w'}^n$  of  $\overline{S}$ . Thus the simplexes of  $\overline{S}$  of vertex  $P_s^k$  satisfy condition (a) of the definition of a star.

(b) Consider first the simplexes of  $\overline{S}$  in  $\alpha_w^n$ .

By definition (1) of regular subdivision any two edges of the subdivision of  $\alpha_w^n$  have either no point or a vertex in common. Hence by definition (2) any two 2-dimensional faces of the subdivision of  $\alpha_w^n$  have either no point or one vertex or one edge in common. Hence by definitions (3), (4), ...,  $(n-1)$  any two  $(n-1)$ -dimensional faces of the subdivision of  $\alpha_w^n$  have either no point or one  $p$ -dimensional face in common,  $(0 \leq p \leq n-2)$ . Finally by definition (n), any two  $n$ -dimensional simplexes of vertex  $P_w^n$  of the subdivision of  $\alpha_w^n$  have one  $p$ -dimensional face in common,  $(0 \leq p \leq n-1)$ .

Consider now two  $n$ -dimensional simplexes  $\overline{\alpha}_1^n$  and  $\overline{\alpha}_2^n$  of  $\overline{S}$  in the simplexes  $\alpha_1^n$  and  $\alpha_2^n$  of  $S_n$ . Then if  $\alpha_1^n$  and  $\alpha_2^n$  have no common point,  $\overline{\alpha}_1^n$  and  $\overline{\alpha}_2^n$  have no common point. If  $\alpha_1^n$  and  $\alpha_2^n$  have in common a  $p$ -dimensional face,  $(0 \leq p \leq n-1)$ , then by definition (n),  $\overline{\alpha}_1^n$  and  $\overline{\alpha}_2^n$  have either no point or a  $q$ -dimensional face in common,  $(0 \leq q \leq p)$  that is  $(0 \leq q \leq p \leq n-1)$ .

Thus any two  $n$ -dimensional simplexes of  $\overline{S}$  have either no point or a  $p$ -dimensional face in common,  $(0 \leq p \leq n-1)$  and in particular any two  $n$ -dimensional simplexes of  $\overline{S}$  of vertex  $P_s^k$  have either no point other than  $P_s^k$  or a  $p$ -dimensional face,  $(1 \leq p \leq n-1)$ , in common.

Thus the simplexes  $\overline{\alpha}_w^n$  of vertex  $P_s^k$  constitute a simplex star of centre  $P_s^k$ .

**Theorem II.** In  $R_n$ , any  $n$ -dimensional simplex star of centre  $A_0$  contains an  $n$ -dimensional spherical region of centre  $A_0$ .

The proof falls into two parts:

(1) If the theorem is true for  $n = (p-1)$ , it is true for  $n = p$ .

(2) The theorem is true for  $n = 1$ .

(1) We assume then that in  $R_{p-1}$ , any  $(p-1)$ -dimensional simplex star of centre  $P_n^k$  contains a  $(p-1)$ -dimensional spherical region of centre  $P_n^k$ . Consider in  $R_p$  a  $p$ -dimensional star  $S_p$  of centre  $A_0$  and let  $U(A_0)$  be a  $p$ -dimensional spherical neighbourhood of centre  $A_0$  and radius  $r$ , where  $r$  is less than the distance of  $A_0$  from any point of the boundary of  $S_p$ . Let  $P_1$  be any point of  $U(A_0)$  in the simplex  $\alpha^p$  of  $S_p$  and  $P_2$  any point of  $U(A_0)$  not in  $\alpha^p$  and not in the line  $P_1 A_0$ . We require to prove that  $P_2$  is in  $S_p$ .

Let  $\alpha_i^i, \alpha_m^j, \dots, \alpha_n^k$ , ( $i, j, \dots, k \leq p-1$ ), be the set of all simplexes, finite in number each of which contains one and only one point of the segment  $P_1 P_2$ . Let  $P_1 P_2$  intersect  $\alpha_i^i, \alpha_m^j, \dots, \alpha_n^k$  in the points  $P_1^i, P_m^j, \dots, P_n^k$  respectively and let  $P_n^k$  be the nearest of these points to  $P_2$ . (Assume  $P_n^k$  to be different from  $P_2$ , for if  $P_n^k = P_2$ , then  $P_2$  is in  $S_p$ ). Since  $U(A_0)$  contains no boundary points of  $S_p$  the simplex  $\alpha_n^k$  containing  $P_n^k$  must be of the form  $A_0 A_1 \dots A_k$ . Let  $\alpha_n^k = A_0 A_1 \dots A_k$  be a  $k$ -dimensional face of the simplex  $A_0 \dots A_k \dots A_p$  of  $S_p$  and let  $A'_1, A'_2, \dots, A'_{p-1}$  be points of  $A_0 A_1, A_0 A_2, \dots, A_0 A_{p-1}$  respectively such that the simplex  $A'_1 A'_2 \dots A'_k$  contains  $P_n^k$  but such that the  $R_{p-2}$  determined by  $A'_1, A'_2, \dots, A'_{p-1}$ , does not contain  $P_2$ . Then the  $R_{p-1}$  determined by  $A'_1, A'_2, \dots, A'_{p-1}, P_2$  contains the segment  $P_n^k P_2$  and intersects  $A_0 A_1$  in one point  $A'_1$  only, so that  $A_0$  and  $A_1$  are on opposite sides of  $R_{p-1}$  in  $R_p$ .

Consider now the intersection of  $R_{p-1}$  and any  $p$ -dimensional simplex  $A_0 A_1 A_{s_2} \dots A_{s_p}$  of  $S_p$  of edge  $A_0 A_1$ . Then  $R_{p-1}$  intersects one of the edges  $A_0 A_{s_i}, A_{s_i} A_1$  in a point  $A'_{s_i}$ . Thus  $R_{p-1}$  intersects the simplex  $A_0 A_1 A_{s_2} \dots A_{s_p}$  in a  $(p-1)$ -dimensional simplex  $A'_1 A'_{s_2} \dots A'_{s_p}$  of vertex  $A'_1$ . The set of such simplexes as  $A'_1 A'_{s_2} \dots A'_{s_p}$  form a  $(p-1)$ -dimensional star  $S_{p-1}$  of centre  $A'_1$  in  $R_{p-1}$ , for they are finite in number and satisfy the conditions (a) and (b) in the definition of a star. Thus:

(a) Because  $S_p$  is a simplex star of centre  $A_0$ , the  $(p-1)$ -dimensional face  $A_0 A_1 A_{s_2} \dots A_{s_{p-1}}$  is common to two and only two

$p$ -dimensional simplexes  $A_0 A_1 A_{s_2} \dots A_{s_{p-1}} A_{s_q}$  and  $A_0 A_1 A_{s_2} \dots A_{s_{p-1}} A_{s_p}$  and thus the  $(p-2)$ -dimensional face  $A'_1 A'_{s_2} \dots A'_{s_{p-1}}$  is common to two and only two  $(p-1)$ -dimensional simplexes  $A'_1 A'_{s_2} \dots A'_{s_{p-1}} A'_{s_p}$  and  $A'_1 A'_{s_2} \dots A'_{s_{p-1}} A'_{s_q}$ . Thus the simplexes  $A'_1 A'_{s_2} \dots A'_{s_p}$  satisfy condition (a).

(b) Any two simplexes of  $S_p$  of edge  $A_0 A_1$  have in common either no point other than the edge  $A_0 A_1$ , or one  $k$ -dimensional face, ( $k = 2, 3, \dots, p-1$ ). Therefore any two of the  $(p-1)$ -dimensional simplexes  $A'_1 A'_{s_2} \dots A'_{s_p}$  have in common either no point other than  $A'_1$ , or one  $k$ -dimensional face, ( $k = 1, 2, \dots, p-2$ ), for if  $A_0 A_1 A_{s_2} \dots A_{s_k}$  is common to two simplexes of  $S_p$ , then  $A'_1 A'_{s_2} \dots A'_{s_k}$  is common to the two corresponding simplexes in  $R_{p-1}$ .

Thus, from (a) and (b) the simplexes  $A'_1 A'_{s_2} \dots A'_{s_p}$  form a  $(p-1)$ -dimensional star  $S_{p-1}$  in  $R_{p-1}$  of centre  $A'_1$ , and we have seen that  $P_n^k$  is in the simplex  $A'_1 A'_2 \dots A'_k$  of  $S_{p-1}$ . Therefore by Theorem I,  $P_n^k$  is the centre of a  $(p-1)$ -dimensional star  $S'_{p-1}$  in  $S_{p-1}$ . Therefore by hypothesis,  $S'_{p-1}$  being in  $R_{p-1}$ , there is a  $(p-1)$ -dimensional spherical neighbourhood  $U(P_n^k)$  of centre  $P_n^k$  in  $S'_{p-1}$ .

If  $P_2$  be in  $U(P_n^k)$  it is in  $S_p$  and our theorem is proved. Consider the case when  $P_2$  not in  $U(P_n^k)$ . Since  $P_n^k P_2$  and  $U(P_n^k)$  are in  $R_{p-1}$ , the segment  $P_n^k P_2$  intersects the boundary of  $U(P_n^k)$  in a point  $Q$  and the segment  $P_n^k Q$  is in  $U(P_n^k)$  and thus in  $S_p$ . Let  $Q$  be in the simplex  $a^q$  of  $S_p$  and note that  $P_2 Q$  contains none of the points  $P_l^i, P_m^i, \dots, P_n^k$ . Since  $P_2$  is in the  $R_q$  containing  $a^q$ , and  $Q$  is in  $a^q$ ,  $P_2$  must be in  $a^q$  for otherwise  $P_2 Q$  would intersect the boundary of  $a^q$  in one point which is impossible (since  $P_2 Q$  contains none of the points  $P_l^i, P_m^j, \dots, P_n^k$ ).

Thus  $P_2$  is in  $S_p$ . Therefore  $U(A_0)$  is in  $S_p$  and the Theorem II is true for  $n = p$ , if it is true for  $n = (p-1)$ .

(2) The Theorem is true for  $n = 1$ , for a 1-dimensional star of centre  $A_0$  in  $R_1$  is a segment of  $R_1$ , and  $A_0$  is an inner point of the segment.

Thus Theorem II is true for any finite  $n$ .

**Mathematics.** — “On the  $n$ -dimensional simplex star in  $R_n$ .” By  
Prof. L. E. J. BROUWER.

(Communicated at the meeting of December 27, 1924).

Each of the two following §§ contains another proof of Mr. WILSON's theorem II deduced in the preceding communication.

### § 1.

Let  $\alpha$  be a  $p$ -dimensional face of an  $n$ -dimensional simplex  $S$  in an  $R_n$ . The flat  $p$ -dimensional spaces of  $R_n$  parallel to  $\alpha$  and having at least one point in common with  $S$  form an  $(n-p)$ -dimensional simplex in the  $R_{n-p}$  of all flat  $p$ -dimensional spaces of  $R_n$  which are parallel to  $\alpha$ .

For let  $P_1, P_2, \dots, P_{n+1}$  be the vertices of  $S$  and  $P_1, P_2, \dots, P_{p+1}$  those of  $\alpha$ . Let  $x_1, x_2, \dots, x_{n+1}$  be barycentric coordinates with respect to  $S$ . Then an arbitrary flat  $p$ -dimensional space of  $R_n$  parallel to  $\alpha$  is given by  $(x_1 + x_2 + \dots + x_{p+1}) : x_{p+2} : \dots : x_{n+1} = a_{p+1} : a_{p+2} : \dots : a_{n+1}$ , the necessary and sufficient condition that it should have at least one point in common with  $S$  laying in the absence of an  $a_\mu$  and an  $a_\nu$  of opposite signs. We may regard these  $a_{p+1}, a_{p+2}, \dots, a_{n+1}$  as homogeneous coordinates of the  $p$ -dimensional spaces considered.

Keeping now the vertices  $P_1, P_2, \dots, P_{p+1}$  unchanged, we replace  $P_{p+2}, \dots, P_{n+1}$  by  $P'_{p+2}, \dots, P'_{n+1}$ , and represent the barycentric coordinates with respect to the new simplex  $S'$  by  $x'_1, x'_2, \dots, x'_{n+1}$ . Then the following formulae of transformation hold:

$$\left. \begin{aligned} x'_1 : x'_2 : \dots : x'_{p+1} : x'_{p+2} : \dots : x'_{n+1} &= (x_1 + {}_1a_{p+2}x_{p+2} + \dots + {}_1a_{n+1}x_{n+1}) : \\ &: \dots : (x_{p+1} + {}_{p+1}a_{p+2}x_{p+2} + \dots + {}_{p+1}a_{n+1}x_{n+1}) : \\ &: ({}_{p+2}a_{p+2}x_{p+2} + \dots + {}_{p+2}a_{n+1}x_{n+1}) : \dots : ({}_{n+1}a_{p+2}x_{p+2} + \dots + {}_{n+1}a_{n+1}x_{n+1}) \end{aligned} \right\} \text{(I)}$$

By means of  $S'$  in the same way as by means of  $S$ , we introduce homogeneous coordinates for the flat  $p$ -dimensional spaces parallel to  $\alpha$  and call these coordinates  $a'_{p+1}, a_{p+2}, \dots, a'_{n+1}$ ; they are evidently homogeneous linear functions of  $a_{p+1}, a_{p+2}, \dots, a_{n+1}$  by the formulae (I).

Thus if in  $R_n$  we have an  $n$ -dimensional simplex star of centre  $P_1$ , having the  $p$ -dimensional face  $P_1 P_2 \dots P_{p+1}$ , then the flat  $p$ -dimen-



sional spaces of  $R_n$  parallel to  $\alpha$  form an  $R_{n-p}$ , and those of them having at least one point in common with any simplex of the star of which  $P_1 P_2 \dots P_{p+1}$  is a face, form in that  $R_{n-p}$  an  $(n-p)$ -dimensional simplex star. For the  $(n-p)$ -dimensional simplexes derived from the  $n$ -dimensional simplexes  $P_1 \dots P_{p+1} P'_{p+2} \dots P'_{n+1}$  and  $P_1 \dots P_{p+1} P''_{p+2} \dots P''_{n+1}$  of the star have always a face in common of as many dimensions as there are indices  $\rho$  for which  $P'_\rho = P''_\rho$ .

We assume now that for  $v < n$ , a  $v$ -dimensional simplex star in  $R_v$  of centre  $C$  fills a neighbourhood of  $C$  in  $R_v$ , and consider a point  $A$  of an  $n$ -dimensional simplex star  $\sigma$  in  $R_n$ , which belongs neither to the boundary nor to a  $(p-1)$ -dimensional face of  $\sigma$ , but to the  $p$ -dimensional face  $\alpha$  of the star, with the vertices  $P_1, P_2, \dots, P_{p+1}$  ( $P_1$  is the centre of the star). Of the set of the flat  $p$ -dimensional spaces of  $R_n$  parallel to  $\alpha$  any neighbourhood of  $\alpha$  fills a neighbourhood of  $A$  in  $R_n$ .

Consequently the set of those flat  $p$ -dimensional spaces of  $R_n$  parallel to  $\alpha$  which cut a simplex of  $\sigma$  of which  $\alpha$  is a face, contain a neighbourhood of  $A$  in  $R_n$  and since the parts of these flat  $p$ -dimensional spaces which lie outside  $\sigma$  have a non-vanishing minimum distance from  $A$ ,  $\sigma$  also fills a neighbourhood of  $A$  in  $R_n$ .

With this property Mr. WILSON's theorem is proved. For, if the closed set  $\sigma$  did not fill a neighbourhood of  $P_1$  in  $R_n$ , there would be a point  $A$  of  $\sigma$  different from  $P_1$ , not belonging to the boundary of  $\sigma$  and being a limiting-point of points of  $R_n$  not belonging to  $\sigma$ .

## § 2.

**Theorem 1.** *Given in  $R_n$  a finite number of flat  $(n-2)$ -dimensional spaces  $l_1, l_2, \dots, l_p$  and two points  $P'$  and  $P''$  not in any  $l_v$  and in a distance  $a$  from each other, then  $P'$  and  $P''$  can be joined by a polygonal path of span  $a$  containing no point of the  $l_v$ .*

**Proof.** Let  $v'$  be the flat  $(n-1)$ -dimensional space through  $P'$  and  $l_v$ , and  $v''$  that through  $P''$  and  $l_v$ . Further let  $P$  be a point of  $R_n$  neither in a  $v'$ , nor in a  $v''$ , but inside the  $(n-1)$ -dimensional sphere of diameter  $P'P''$ . Then the segments  $P'P$  and  $PP''$  constitute a polygonal path satisfying the required conditions.

**Theorem 2.** *Let  $S$  be an  $n$ -dimensional simplex star in  $R_n$ ,  $b$  the intrinsic boundary of  $S$  (i. e. the set of points formed by those faces of  $S$  not having the centre of  $S$  as vertex),  $K$  a point of  $S$  not belonging to  $b$ ,  $G$  the domain complementary to  $S$  in  $R_n$ , and  $g$  the boundary (obviously belonging to  $S$ ) of  $G$  in  $R_n$ . Then  $K$  can not belong to  $g$ .*

Proof. A point of  $S$  belonging neither to  $b$  nor to an  $(n-2)$ -dimensional face of  $S$  has always a neighbourhood (with respect to  $R_n$ ) laying entirely in  $S$ . Consequently  $g$  is the sum (union) of  $b$  and a closed set of points  $c$  entirely in the  $(n-2)$ -dimensional faces of  $S$ . Let  $d$  be the distance (measured in  $R_n$ ) of  $K$  from  $b$ .

Assume now that  $K$  belongs to  $g$ . In that case at a distance  $< \frac{1}{4}d$  from  $K$ , there could be assigned on the one hand a point  $P'$  of  $G$  and on the other a point  $P''$  belonging to  $S$  but not to an  $(n-2)$ -dimensional face of  $S$ . By theorem 1,  $P'$  and  $P''$  could then be joined by a polygonal path  $\pi$  of span  $< \frac{1}{2}d$  not meeting  $c$ , which, just because its span is  $< \frac{1}{2}d$ , also would not meet  $b$  and thus would have no point in common with  $g$ . But this result is contradictory, since  $\pi$  joins the point  $P'$  of  $G$  to the point  $P''$  not in  $G$ . The assumption that  $K$  belongs to  $g$  is thus reduced to an absurdity proving theorem 2.

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**Botany.** — “*The Results of the Temperature during flower-formation for the whole Hyacinth*”. (Second Part). Laboratory for plant-physiological Research, N°. 11, Wageningen, Holland). By A. H. BLAAUW.

(Communicated at the meeting of September 27, 1924).

§ 10. *Had the different temperature-treatments a noticeable influence on the growing-point formed during that period?*

In connection with the results discussed in the first part (Verh. Kon. Akad. v. Wet. 2<sup>nd</sup> section. Part XXIII N°. 4; §§ 1—9), there were many questions to be answered. They have partly been solved in the cultural year 1923—1924 and will be briefly communicated in this paper.

The results of 44 different temperature-treatments were described in part I. Where-ever a flower-cluster was formed under a certain treatment (whether this cluster became a failure or not) the new growing-point was also formed. This new growing-point which is to form a flower-cluster a year later and to flower next April twelvemonth, originated and grew during the first weeks that is under very different temperature-conditions.

Now the question is, whether those different temperatures have a noticeable influence on this new bud and the flowering plant arising from it.

For this purpose the circa 20 bulbs of each of the 44 experiments were treated *all in the same way* during the summer of 1923, i.e. from the beginning of July to Sept. 1 in 25° to 26°, from Sept. 1 to planting-time in 17°, which is the optimal treatment for flower-formation as hitherto *approximated*.

But the material was, as communicated before, far from uniform after the 44 treatments. I refer to the weight of the bulbs, which at the end of the experiments previously described (July 1923) had become as shown in table 21. This should be taken into consideration when judging the results. (See table 21 next page).

Secondly we should bear in mind that in some extreme treatments there was not formed any flower-cluster at all and the same growing-

point was retained. In that case no new growing-point has been formed in that temperature; only the existing growing-point which was to form a flower-cluster next year, has experienced that temperature. This is quite an other matter than the formation of a new growing-point in a certain temperature, because on retention of the same growing-point in consequence of extreme temperatures, processes of growth and division are fairly brought to a standstill.

TABLE 21. Average weights of the bulbs at the beginning of July 1923 in grams per bulb, after having been *variously* treated in the *summer* of 1922 and before being *uniformly* treated in the *summer* of 1923.

Temp.	3 w.	5 w.	8 w.	12 w.
1½°	18.0	15.7	11.2	8.5
5°	17.7	17.2	11.9	8.9
9°	19.4	17.3	15.8	8.9
13°	23.3	20.5	18.5	14.9
17°	22.9	21.5	19.1	22.9
20°	23.0	24.7	25.0	22.9
23°	25.8	27.2	30.4	28.9
25½°	30.4	27.6	31.6	29.2
28°	28.8	30.2	29.0	29.5
31°	26.6	29.7	30.8	20.9
35°	31.1	40.6	38.2	23.4

Table 15 part I already shows that (judged per 10 bulbs in January) in 1½°, 5°, 35° during a 12 weeks' treatment the same growing-point was nearly always retained (in 9 or 10 of the 10 bulbs). Consequently after 8 or 5 or 3 weeks' treatment there usually has not been formed a flower-cluster in those temperatures and the same growing-point has been retained. The flower-cluster and new growing-points found, *after* 8, 5 or 3 weeks' treatment in 1½°, 5°, 35° still generally occurring, *are formed under the influence of the further treatment in 17°*. Let us subject fig. 2 part I to a closer examination. It shows us that only in temperatures from 13° up to and inclusive of 31° all or the greater part of the growing-points form a cluster, so a new growing-point; in 1½°—5°—9° and 35° only less than half the number or an exceptional



few. (If stage III is reached (first indication of the first 1 or 2 flower-primordia) the young growing-point at the base is *always* present. We must allow for the fact, that with those bulbs which were treated a year before in  $1\frac{1}{2}^{\circ}$ ,  $5^{\circ}$ ,  $9^{\circ}$ , and  $35^{\circ}$  *as a rule the new growing-point was not formed in those temperatures*, but that either the old growing-point was retained, (usually in  $1\frac{1}{2}^{\circ}$ ,  $5^{\circ}$  and  $35^{\circ}$ , after 12 weeks' treatment) or a new growing-point was formed later on in lower temperatures (in the rooms in  $17^{\circ}$  or even after planting in the garden in October). As chief result it may be mentioned, that in the material of these bulbs *grown later* under equal circumstances, not any particular deviation occurred in the flower-clusters (or other organs). Of course there appeared in the heavier more compact clusters occasional deviating flowers as may always be found under normal treatment on large clusters. The influence of temperatures from  $13^{\circ}$  to  $31^{\circ}$  during bud-formation led to no sort of deviation in the flower-clusters, which arose from these growing-points the next year. No more in the few specimens which this new growing-point will have formed in  $35^{\circ}$  or  $9^{\circ}$ . This however proves by no means, that it would be impossible to effect constant lasting *bud-variations* by brief exposures to strong heat or to increase the chance of causing them. This chance however does not seem great to me.

The flowering of this field of Hyacinths, with uniform treatment during the last year, but after so dissimilar a treatment in the preceding summer, was quite uniform. The size of the clusters diverged greatly, but was normally dependent upon the size of the planted bulbs. A table of the most diverging groups will suffice.

TABLE 22.

I.	II.	III.	IV.	V.	VI.	VII.
Treatment summer 1922	Weight July 1922 per bulb	Weight July 1923 per bulb	Treatment summer 1923	Numbers of flowers April 1924 per bulb	Number of leaves p. 10 bulbs in 1924	Weight July 1924 per bulb
$35^{\circ}$ 5 weeks	11.8 grs.	40.6 grs.	$25\frac{1}{2}^{\circ}$ 8 weeks $17^{\circ}$ $4\frac{1}{2}$ weeks	29.2	56	54.0 grs.
$35^{\circ}$ 8 "	11.7 "	38.2 "		23.4	54	51.2 "
$25\frac{1}{2}^{\circ}$ 8 "	11.4 "	31.6 "		18.3	49	40.0 "
$9^{\circ}$ 12 "	11.5 "	8.9 "		4.8	40	22.0 "
$5^{\circ}$ 12 "	11.5 "	8.9 "		3.8	39	19.8 "
$1\frac{1}{2}^{\circ}$ 12 "	11.5 "	8.5 "		0	33	19.3 "

From this it appears: 1°. When in 1922 no cluster was formed ( $9^{\circ}$ — $5^{\circ}$ — $1\frac{1}{2}^{\circ}$  12 weeks), this did not benefit the leaf-formation. The number of leaves, assimilating the next year was normally small with regard to the circumferences of the bulbs, which also remained small (see column VI). 2°. The number of leaves on the cluster was the greater according as the bulbs were heavier in the beginning of the cultural year (columns III and VI); so that also at the end the same order of succession in bulb-weight was maintained (column VII), while those bulbs which had lagged behind, vigorously made up for lost time. 3°. The number of flowers (col. V) was likewise in accordance with the weight of the bulbs (col. III). The bulbs which after a previous treatment in  $1\frac{1}{2}^{\circ}$  for 12 weeks had been reduced from 11.5 to 8.5 grs did not flower, of those from  $5^{\circ}$  (reduced to 8.9. grs) 8 of the 18 plants flowered with very poor clusters (average  $3\frac{3}{4}$  flowers). This is quite as might be expected of a similar bulb-weight (or bulb-circumference). We are here on the limit of flowering-ability, to which subject I shall revert in a next paper. Those which had previously been in  $9^{\circ}$  produced 16 clusters on 21 plants, with an average of  $4\frac{3}{4}$  flowers. While the average bulb-weight in *both* these groups (see table 21) was 8.9 grams, it appears that the previous treatment in  $5^{\circ}$  is still a little more unfavourable in its after-effect than  $9^{\circ}$ . 4°. It is of more importance that the bulbs treated a preceding year in  $35^{\circ}$  for 5 or 8 weeks had normally full clusters according to their circumferences, larger clusters therefore than those which received an optimal flower-treatment the year before. It should be borne in mind, as described in part I, that the leaf-optimum, i. e. the optimum for circumferential bulb-increase, lies much higher than for flower-formation, viz. in a temperature very unfavourable to flower-formation. Practically in the first years when the clusters are of no consequence, a high temperature might be applied and only later on  $\pm 26^{\circ}$  might be used with a view to flower-formation. But it had not yet been ascertained whether bulbs one year treated in  $35^{\circ}$  and giving no or bad clusters and beautiful foliage, could yield optimal clusters in  $26^{\circ}$  the next year. This now appears to be the case. After a treatment in  $35^{\circ}$  for 8 weeks in 1922 there appeared 3 clusters on 30 plants in April 1923; after optimal flower-treatment in the summer of 1923 all of these bulbs produced clusters with an average of 23 flowers in 1924 (in their 4<sup>th</sup> year, circumference 12 to 13 cms). See further table 22.

On the optimal foliage-treatment various experiments are being made, but it is certain, *that after optimal foliage-treatment optimal flower-treatment may be successfully started the next year.*

§ 11. *A control of the optimal temperature found for one year older bulbs.*

The experiments discussed in part I were made on young newly flowering bulbs, for reasons mentioned there. The optimal temperature found for the plant in general and particularly for the flower-cluster was now checked for a year older bulbs (circumference 120 to 130 mms at the beginning of July 1923). So these bulbs have been judged in the course of their fourth year. As to their size trade would class them as miniatures. But while the bulbs of the previous experiments were only just capable of flowering, these bulbs have passed that limit. For this control-experiment I preferred *one year older bulbs*, because the variation in number of flowers on the cluster is not yet so great, because not so many abnormal flowers occur as in the more compact clusters and lastly because the bulbs of this variety in their fourth year increase in size more uniformly than in older years.

Bulbs were chosen of a circumference (beginning of July) from 120 to 130 mms. In this experiment only the temperature-optimum was checked, not the period during which the temperature influenced. Thus 30 bulbs were kept in  $17^{\circ}$ — $20^{\circ}$ — $23^{\circ}$ — $25\frac{1}{2}^{\circ}$ — $28^{\circ}$  and (25 specimens) in  $31^{\circ}$  for 8 weeks and next  $4\frac{1}{2}$  weeks in  $17^{\circ}$ . This was to serve as a control for the *flower-optimum* hitherto approximated ( $25\frac{1}{2}^{\circ}$  8 weeks +  $4\frac{1}{2}$  weeks  $17^{\circ}$ ). On the *foliage-optimum* further details will be given in a later paper.

After the treatment on planting (4 Oct. 1923) the average weight of these six groups ( $17^{\circ}$  to  $31^{\circ}$ ) was 27.3—27.9—27.0—27.8—28.0 and 28.6 grams resp. I shall presently revert to this, but I mention here, that since the summer of 1924 we do not only make an accurate selection of the bulbs according to their circumference, but we also divide the various groups of each series of experiments into equal weights. Consequently the difference between the groups to be compared becomes still smaller, the comparison more accurate.

The *root-whorl* (beginning of Oct.) was least visible after treatment in  $17^{\circ}$ , a little more in  $20^{\circ}$ , a little farther in  $23^{\circ}$ , better in  $25\frac{1}{2}^{\circ}$ , in  $28^{\circ}$  and  $31^{\circ}$  most advanced, fairly uniform, very good, almost alarmingly long for planting (beginning of October).

As to *showing above ground* (this refers to leaf-length) those from  $25\frac{1}{2}^{\circ}$ — $28^{\circ}$ — $31^{\circ}$  were most advanced and fairly equal, those from  $23^{\circ}$ — $20^{\circ}$  and  $17^{\circ}$  were advanced in a lessening degree.

As to *coming into bloom*  $25\frac{1}{2}^{\circ}$  is farthest,  $28^{\circ}$  about equally far,

next 23° and 31° much less advanced, 20° behind 31°, but more vigorous, 17° less far and less favourable than 20°.

TABLE 23. *Number of clusters (numerator) with respect to the number of plants (denominator), and the number of flowers on the succeeded clusters, both of these bulbs in their fourth year and of a year younger bulbs.*

	17°	20°	23°	25½°	28°	31°
Succeeded clusters (bulbs 12—13 cms)	30/30	30/30	30/30	29/30	30/30	25/25
Idem on bulbs of 8—9 cms	12/30	24/30	28/30	30/30	27/30	27/30
Average numbers of flowers per cluster on bulbs of 12—13 cms.	<b>13.50</b> <i>m</i> ± 0.48	<b>14.47</b> <i>m</i> ± 0.43	<b>14.93</b> <i>m</i> ± 0.49	<b>16.24</b> <i>m</i> ± 0.38	<b>15.30</b> <i>m</i> ± 0.35	<b>11.12</b> <i>m</i> ± 0.32
Idem on bulbs of 8—9 cms	<b>6.07</b> ± 0.23	<b>5.57</b> ± 0.14	<b>6.0</b> ± 0.18	<b>5.57</b> ± 0.18	<b>5.68</b> ± 0.25	<b>3.15</b> ± 0.28

From this it appears that as contrasted with the younger bulbs, these older ones without an exception produce a flower-cluster after treatment in 17° to 31°. With the younger ones only 12 of the 30 bulbs yielded a flower-cluster after a treatment in 17°. This proves that bulbs from 8 to 9 cms are so much closer to the limit of flowering-ability, that it requires a so much more delicate treatment to make them all produce flowers than larger bulbs.

As far as the cluster succeeds with the smaller bulbs, the number of flowers per cluster is fairly equal after the various temperatures, as is already discussed in part I; only in 31° a smaller number was found, which, considering the slight mean error (*m*), is certainly not due to chance.

With the greater bulbs a slight rise is found from 17° to 25½°. Though the difference between 2 succeeding temperatures is slight, so that the mean error might explain the difference, the fact that this rise gradually progresses till 25½° and next decreases first slowly, in 31° however faster, shows that these differences are certainly not due to chance.

The strong decrease in 31° (5 flowers per cluster or ca ⅓ of the number after treatment in 25½°) is corroborated on the older bulbs, while likewise in this case 25½° is most favourable with regard to



the number of flowers. It cannot be attributed to an unfavourable influence of this temperature, that one cluster is lacking on 30 plants; with the *younger* bulbs all bulbs happened to bear a cluster after that treatment.

Lastly it should be mentioned that after treatment in  $31^{\circ}$  a great many abnormal flowers occurred in the clusters, in spite of the fact, that the clusters were rather poor in flowers. These abnormalities caused by abnormal circumstances will be discussed later on in connection with the material collected in these years.

The experiments discussed in this § are only meant as a check on the optimal temperature for flowering in a year older bulbs. The result is a corroboration that a *treatment in  $25^{\circ}$ — $26^{\circ}$*  (for 8 weeks) is most *favorable*.

The experiment did not aim at leaf-surface and circumferential increase of the bulb, which will be discussed later on. In that discussion however the data of this experiment may be of use to us; hence I will communicate something about them here.

TABLE 24. Number of assimilating leaves shooted in April 1924 after a treatment in  $17^{\circ}$ — $31^{\circ}$  July to Aug. 1923.

	$17^{\circ}$	$20^{\circ}$	$23^{\circ}$	$25\frac{1}{2}^{\circ}$	$28^{\circ}$	$31^{\circ}$
Number of leaves:	$\left\{ \begin{array}{l} 10 \times 3 \\ 16 \times 4 \\ 4 \times 5 \end{array} \right.$	$\left\{ \begin{array}{l} 4 \times 3 \\ 12 \times 4 \\ 14 \times 5 \end{array} \right.$	$\left\{ \begin{array}{l} 17 \times 5 \\ 13 \times 6 \end{array} \right.$	$\left\{ \begin{array}{l} 4 \times 5 \\ 24 \times 6 \\ 2 \times 7 \end{array} \right.$	$\left\{ \begin{array}{l} 3 \times 5 \\ 26 \times 6 \\ 1 \times 7 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \times 5 \\ 26 \times 6 \\ 3 \times 7 \end{array} \right.$
Average p. 10 bulbs	38.0	43.3	54.3	59.3	59.3	60.7
$m =$	$\pm 1.2$	$\pm 1.3$	$\pm 0.9$	$\pm 0.8$	$\pm 0.65$	$\pm 0.65$

It is again corroborated on these bulbs, that *high temperatures are needed for a subsequent shooting of all young leaflets ready in the beginning of July*: After  $25\frac{1}{2}^{\circ}$ ,  $28^{\circ}$ ,  $31^{\circ}$  the average 6 leaflets formed all get to assimilation later on; already after  $23^{\circ}$  not all of them unfold, after  $20^{\circ}$  and  $17^{\circ}$  a great number of them is arrested. Observe the very slight mean error and compare these data with the result given in part I § 3 A Tab. 2. In those younger bulbs of 8 to 9 cms circumference in July there succeeded:

25    31    35<sup>1)</sup>    40    39    41 leaves resp.

of the ca 40 leaves formed per 10 bulbs after that same treatment.

<sup>1)</sup> 45 instead of 35 in part I is due to a printer's error.

TABLE 25. The *average leaf-length* in mms. (longest leaf, average of 30 bulbs, inclusive of the ca. 80 mms. below the surface of the soil) amounted in the beginning of June to:

17°	20°	23°	25½°	28°	31°
343	356	370	373	388	402

We notice a slight rise according as the temperature was higher. In the younger bulbs we found the foliage-length about equal from 23° to 31° and only much increased in 35°. The favorable effect of a very high temperature on the leaf surface is corroborated here at any rate. In connection with this I add the increase in weight.

TABLE 26. Increase in weight per bulb with initial weight (July 1923) and final weight (July 1924) after a treatment in July and Aug. 1923 in:

17°	20°	23°	25½°	28°	31°
34.1 } 44.7 } 10.6	34.9 } 45.0 } 10.1	33.8 } 48.0 } 14.2	34.8 } 48.6 } 13.8	35.0 } 50.5 } 15.5	35.5 } 59.7 } 24.2

On the whole this increase in weight is not great in comparison with the younger bulbs, *but a strong increase of the assimilation-effect is already attained by 31° and consequently corroborated for high temperatures.* Later on this will be discussed in detail, because the relation between bulb-circumference, bulb-weight and annual "normal" increase in weight and circumference require a separate treatment. The cause of the rather slight increase in the moderate temperatures may also be due to the fact that in the very late spring of 1924 flowering and assimilation commenced in the experimental grounds *more than 3 weeks later* than in 1923; whereas the assimilation after the sunny months of May and June 1924 was finished earlier than after the wetter early-summer of 1923.

§ 12. *May the approximated optimum be perceptibly improved by exposure to a temperature still higher than 25½°, soon after lifting?*

In the following §§ the question is discussed whether the approximated optimal treatment for the flowering plant might be improved. This subject will be continued in a subsequent paper. After lifting

8 weeks in  $25\frac{1}{2}^{\circ}$ , then till planting-time  $4\frac{1}{2}$  weeks in  $17^{\circ}$  is the optimal combination hitherto approximated.

May the effect be improved by exposure to a higher temperature than  $25\frac{1}{2}^{\circ}$  in the beginning after lifting for a shorter or longer period? As the effect of  $28^{\circ}$  and  $25\frac{1}{2}^{\circ}$  was not very different, I preferred to use  $31^{\circ}$  as a higher initial temperature, seeing that otherwise no difference worth mentioning might be expected.

While the control-group remained in  $15\frac{1}{2}^{\circ}$  for 8 weeks, 5 other groups were put in  $31^{\circ}$  the 1<sup>st</sup>, the 2<sup>nd</sup>, the 3<sup>rd</sup>, the 1<sup>st</sup> + 2<sup>nd</sup> and the 2<sup>nd</sup> + 3<sup>rd</sup> week resp. and for the rest kept in  $25\frac{1}{2}^{\circ}$  after 8 weeks in  $17^{\circ}$ . Each group also the control-group contained 40 bulbs of 80 to 90 mms circumference. Moreover each group was divided into two in order to find out whether a difference worth mentioning was obtained, when *the planting took place after only  $2\frac{1}{2}$  weeks in  $17^{\circ}$  or in the beginning of October after  $4\frac{1}{2}$  weeks' stay in  $17^{\circ}$ .*

So the experiments discussed in this § refer to two different questions. The groups planted after  $2\frac{1}{2}$  weeks  $17^{\circ}$  and after  $4\frac{1}{2}$  weeks  $17^{\circ}$  resp. will be indicated "earlier" and "later".

The *root-whorl* on Oct. 4 is not perceptibly different in the groups 'later'.

On *showing above ground* (leaf-length) March 24, 1924 (very late spring after long winter) 1<sup>st</sup> + 2<sup>nd</sup> week  $31^{\circ}$  and 2<sup>nd</sup> + 3<sup>rd</sup> week  $31^{\circ}$  are more advanced both in the earlier and in the later groups, however but little farther than the control-group; — on the other hand 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> week  $31^{\circ}$ , both earlier and later planted, are somewhat behind the control-group.

*1<sup>st</sup> + 2<sup>nd</sup> week  $31^{\circ}$  or 2<sup>nd</sup> + 3<sup>rd</sup> week  $31^{\circ}$  have a slight advantage over the control-group as concerns the foliage-length when showing above ground. Planted "earlier" however does not mean showing above ground "earlier"; "later" on the contrary means a greater uniformity.*

Also as to *flowering* with those planted later the 1<sup>st</sup> + 2<sup>nd</sup> and 2<sup>nd</sup> + 3<sup>rd</sup> week  $31^{\circ}$  are somewhat more advanced than the control-group (with those planted earlier the groups are equal as to rate of flowering). — (It should be borne in mind that in a long winter slight differences in the flowering-period are easily effaced).

Soon after lifting the leaf-formation ceases and the growing-point is raised and is about to form flowers. So the treatment described here might easily influence the number of flowers.

The average number of flowers per cluster amounts to ca 6, and corresponds with the findings on equally large bulbs the previous

TABLE 27. Number of flowers per cluster, as an average of ca. 20 plants. As planting a fortnight earlier or later can have no influence on the number of flowers, those results may be taken together.

Control earlier	6.20	$m = \pm 0.28$
Control later	6.10	$m = \pm 0.22$
1st week 31° earlier	5.90	$\pm 0.33$
1st week 31° later	6.16	$\pm 0.31$
2nd week 31° earlier	6.76	$\pm 0.34$
2nd week 31° later	6.05	$\pm 0.20$
3rd week 31° earlier	6.80	$\pm 0.29$
3rd week 31° later	5.80	$\pm 0.29$
1st + 2nd week 31° earlier	5.95	$\pm 0.26$
1st + 2nd week 31° later	5.95	$\pm 0.20$
2nd + 3rd week 31° earlier	5.94	$+ 0.20$
2nd + 3rd week 31° later	5.60	$\pm 0.24$

year with the same treatment (see table 19 part I) or may be a little more favorable.

Between the various experiments no difference is to be ascertained with certainty: 2<sup>nd</sup> week 31° "earlier" (6.76) seems, considering the mean error, somewhat higher, but those planted later (6.05) are "normal"; likewise 3<sup>rd</sup> week 31° earlier (6.80) is rather high, but those planted later (5.80) are again fairly low. As planting on Sept. 17 or Oct. 2 cannot affect the number of flowers of a cluster each two groups may be taken together.

The conclusion must be that the number of flowers is not altered worth mentioning by the treatment described; perhaps it decreases slightly in the 2<sup>nd</sup> + 3<sup>rd</sup> week 31°.

As in 31° the flower-formation is much inhibited the first 3 weeks also therefore the 1<sup>st</sup> + 2<sup>nd</sup> week (see fig. 2 part. I), it is a remarkable fact, that in spite of this about the same number of flowers is attained, and this very group 1<sup>st</sup> + 2<sup>nd</sup> week 31° (likewise 2<sup>nd</sup> + 3<sup>rd</sup> week 31°) is flowering yet a little earlier in spring.

The differences however are so slight, that with respect to optimal flowering the optimum already found may be maintained; with respect



to *celerrimal* flowering a small advantage in time might be gained by beginning the 1<sup>st</sup> and 2<sup>nd</sup> week (not longer) with e.g. 28° to 30° C. in stead of 25° to 26° C. We shall revert to this in a later paper on early-flowering; it may be of some interest for early-flowering and I will not omit pointing out that as to the first couple of weeks we arrive at the same temperature with which practice starts in preparing for early-flowering. As I already demonstrated before e.g. l'Innocence does not require lifting earlier than at the normal point of time provided a *suitable* treatment follows.

The number of leaves shootd normally in all experiments, as might be expected on exposure to 25½°, and 31°. Neither did the increase in weight yield special phenomena. It amounted to *ca* 16 grams per bulb from July 1923 to July 1924 in most groups. This corroborates our supposition with respect to the other bulbs at the end of § 11, for the bulbs of these experiments can be directly compared as to age and size with the experiments from part I, where the increase in weight from July 1922 to July 1923 amounted to *ca* 20 grams per bulb after optimal flowering-treatment. (See table 8). Meantime these experiments have not been directed at optimal increase in weight; as has already been demonstrated a greater increase in weight can be attained by an other treatment.

§ 13. *Is it desirable that the transition from a higher (25½°,) to a lower temperature (17°) should take place before or after 8 weeks?*

Hitherto as an optimal treatment for flowering 8 weeks 25° to 26°, next 17° till planting-time was found. In these experiments however (part I) long intervals of time were taken, and 3 weeks, 5 w., 8 w. and 12½, w. in 25½°, (for the rest 17° or planting at once after 12½, weeks) were compared. 8 weeks proved most successful for the plant as a whole and particularly for the flower-cluster. The difference between 5 w. and 8 w. was not very great, between 8 and 12 weeks easily perceptible and showing itself in an injurious effect of a prolonged stay in a high temperature. Now it might be desirable to make that high temperature last a little shorter or longer than 8 weeks before transmitting the bulbs to 17°.

For this purpose 20 bulbs of 80 to 20 mms were kept 6, 7, 8 and 9½, week resp. in 25° to 26° C. and next transferred to 17° C. Can a difference or advantage worth mentioning be gained upon 8 weeks 25½°,?

In the *root-whorl* no difference is visible in the beginning of Oct., or may be 6 and 7 weeks a little more advanced.

On *showing above ground* all four groups are equal; 8 and 9 weeks a little more uniform and vigorous.

As to *coming into bloom* 6 weeks is most advanced, 7 and 8 weeks equal, especially 9 weeks perceptibly later.

This corroborates the celerrimum of flowering (table 18 part I), where 5 weeks  $25\frac{1}{2}^{\circ}$  were obviously earlier as to flowering than 8 weeks  $25\frac{1}{2}^{\circ}$ .

I have availed myself of this experience in my experiments with respect to early-flowering (celerrimal flowering) when already after 5 weeks the high temperature is abandoned. On the correct temperature thereafter experiments are being made.

TABEL 28. Number of flowers, number of leaves, increase in weight after 6, 7, 8 and 9 weeks  $25\frac{1}{2}^{\circ}$ .

$25\frac{1}{2}^{\circ}$	Number of flowers per cluster	Assimilating leaves per 10 plants	Increase in weight per bulb in grams (July '23—July '24)
6 weeks	6.50 $\pm$ 0.23	35 $\pm$ 1.3	11.5
7 weeks	5.95 $\pm$ 0.22	38 $\pm$ 0.9	10.35
8 weeks	7.26 $\pm$ 0.37	38 $\pm$ 0.9	13.75
9 weeks	6.50 $\pm$ 0.27	37 $\pm$ 0.1	12.8

The number of shooting leaves appears, considering the slight mean error, to slightly decrease in 6 weeks (this surely was the case in 5 weeks  $25\frac{1}{2}^{\circ}$  the year before). With this group the increase in weight is slight, obviously less than with the experimental plants discussed in § 12 which were equally large and grown in the same frame with equal groundwater-level. It appears how cautious we must be in comparing the increase in weight of various experimental series and how necessary it is to place the groups to be compared of one experimental series as close together as possible. Comparison of the 4 groups one with another (table 28) shows that the increase in weight in the 8 weeks' experiment is the most favourable at any rate.

As to the number of flowers per cluster, 6, 7 and 9 weeks yield the normal average of a little over 6 flowers per cluster, considering the mean error. Only 8 weeks (7.26) shows a slightly higher average

which can hardly be attributed to chance. On the whole the number of flowers in this series is slightly higher than with the equally large and equally old bulbs of table 27 and so the result of 8 weeks is somewhat more favorable than with the control-specimens of table 27 which were treated in the same way. The question is whether any value may be attached to this, but it is certain that it appears from this more detailed experiment, that with respect to optimal treatment for flower-clusters 8 weeks  $25\frac{1}{2}^{\circ}$  remains to be recommended, only after that a cooler temperature.

Separating into 6, 7, 8, 9 weeks was of so great an interest, because it was the way to answer the question, how long a high temperature is permitted and necessary with regard to the flower-cluster. On regarding the formation even in the small clusters after 8 weeks, we notice that in the basal flowers the formation of the various organs is nearly always ready (see fig. 2 part I), and the basal couple of flowers was always used as a criterion for the stage of development.

The top-flowers also on these poor clusters are not so far advanced after 8 weeks, and so the question rose, whether it would be a perceptible advantage to the number of flowers, if about that time the high temperature was continued longer or shorter than 8 weeks. This appears not to be the case. It is of great importance to know when that cooler temperature had better begin. We started exposure to the high temperature on July 5<sup>th</sup> to 7<sup>th</sup>, directly after lifting and so got to "8 weeks", or ca Sept. 1. But the bulbs may be lifted later, when the beginning of the summer is wet, or they may be lifted earlier and treated differently with a view to early-flowering; moreover with early-flowering varieties as l'Innocence the cluster-formation probably will be sooner finished. The expression "Sept. 1" or even "after 8 weeks" does not suffice. More objectively, less blindly or at random, it should be mentioned in what condition the top-flowers were at the period which appeared to be most favourable for a transition from hot to cooler temperature. A more detailed discussion of this point will be given in the next paper. From observations made by Mr. WOLLRING in our laboratory I can communicate that with this treatment in the greater part of the top-flowers at the most favourable time of transmission to  $17^{\circ}$  the primordia of the outer whorl of stamens have been formed, so that the top-flower was in stage VII (see part I § 6 A). When the top-flower has advanced no farther than this in the formation of the flower-parts, a transition to a lower temperature may be effected without risk, so that the flower still fully develops and unfolds.



*A longer stay in that high temperature yields no advantage, e. g. it does not give rise to the formation of more flowers by the vegetation-point.*

When we aim at *early-flowering* (celerrinal flowering) the high temperature may be discontinued earlier when a suitable treatment till the flowering-period follows. To the question in what stage the top-flowers should be for early-flowering before we pass on to a lower temperature, we shall revert in a later article.

§ 14. *Is a transition from the higher temperature ( $23^{\circ}$ ,  $25\frac{1}{2}^{\circ}$  or  $28^{\circ}$ ) after 8 weeks to a temperature lower than  $17^{\circ}$ , e. g.  $13^{\circ}$ ,  $9^{\circ}$  or  $5^{\circ}$  desirable?*

In the experiments discussed in part I the bulbs were transferred to ca  $17^{\circ}$  C. from 11 different temperatures after 4 different periods. This temperature was originally chosen somewhat at random. After the experiences obtained it appeared, e. g. when the bulb was treated in  $20^{\circ}$  for 8 weeks that a transition to  $17^{\circ}$  was better than a continued exposure to  $20^{\circ}$  for the remaining  $4\frac{1}{2}$  weeks. From this it followed, that with a view to the after-treatment there was little occasion to expect the approximation of the optimal treatment above  $17^{\circ}$ . It being not possible and desirable to make and judge more time- and temperature-combinations simultaneously, experiments were made in a second year to investigate the possibility of improving the initial approximated optimum by passing from the high temperature not only to  $17^{\circ}$ , but also to  $13^{\circ}$ ,  $9^{\circ}$ , and  $5^{\circ}$ . Though  $25^{\circ}$  to  $26^{\circ}$  had appeared to be best for the treatment for 8 weeks in the higher temperature and an after-treatment in  $17^{\circ}$ , yet it seemed advisable to me to expose to  $23^{\circ}$  and  $28^{\circ}$  by the side of  $25\frac{1}{2}^{\circ}$ , because it might be possible, that the combination e.g. of  $28^{\circ}$  with e.g.  $13^{\circ}$  or  $9^{\circ}$  might yield a better result than of  $25\frac{1}{2}^{\circ}$  with  $17^{\circ}$  or lower.

Thus 12 experiments each with 30 bulbs measuring 80 to 90 mms (at the end of their second year) were made, the material of which was exposed to  $23^{\circ}$ ,  $25\frac{1}{2}^{\circ}$ , and  $28^{\circ}$  for 8 weeks and next  $17^{\circ}$ ,  $13^{\circ}$ ,  $9^{\circ}$  and  $5^{\circ}$  till the beginning of October. Then 10 specimens were fixed and the remaining 20 planted in concrete frames with a 60 cms ground-water-level in common mould of our ground, for the rest manured and mixed with lime in the same way as trade prepares a good Hyacinths plot.

The *root-whorl* is farthest advanced and in both cases about equal after  $25\frac{1}{2}^{\circ}$ — $17^{\circ}$  and after  $28^{\circ}$ — $17^{\circ}$  in October. Next from  $17^{\circ}$  to



5° the progress of the root-whorl is perceived to diminish. At the end of the temperature-treatment, 10 specimens were at once fixed in order to ascertain the *direct effect* of the 12 treatments.

TABLE 29. Length of the 1st, 2nd and 3rd foliage-leaf and height of the cluster on Oct. 5th 1924.

	Length 1 Sept.	5°	9°	13°	17°
1st Leaf	23°	6.0	13.0 ( $\pm 0.15$ )	16.9 ( $\pm 0.23$ )	19.3 ( $\pm 0.19$ )
	25½°	5.9	11.7	17.1	19.5
	28°	5.4	9.8	17.3	19.1
2nd Leaf	23°	—	11.1	15.1	17.2
	25½°	—	9.8	15.4	17.2
	28°	—	8.6	15.8	17.0
3rd Leaf	23°	—	9.5	12.9	15.0
	25½°	—	7.3	13.6	15.5
	28°	—	7.2	13.8	15.2
Cluster	23°	2.5	5.9 ( $\pm 0.54$ )	9.9 ( $\pm 0.38$ )	11.6 ( $\pm 0.46$ )
	25½°	2.6	4.6	9.7	11.9
	28°	1.9	4.2	9.0	12.1

The lengths of the second and third leaves were also measured in order to have a better control on the effect of the young leaflets in the slight number of 10 specimens. Only in the case of 23° 1<sup>st</sup> leaf and flower-cluster the mean error was computed and added, in order to get an impression of the amount of the mean error in these experiments. On the whole it may be observed, that this is slight for so small a number of observations (10), that the variation in length of these young organs is not great. The length of the 1<sup>st</sup> leaf and of the cluster on Sept. 1, i.e. at the period of transition from 23°—25½° and 28° to a cooler temperature has been added as far as it was known.

From this table it may be concluded:

1. An after-treatment in 9° and 5° yields a distinctly slighter length of leaflets and flower-cluster than 13° and 17°.

2. As to 5° it is striking that the inhibition is less according as the preliminary treatment was less warm. As already on Sept. 1, 23° is

more advanced in length than  $28^{\circ}$ , it might be concluded, that in that low temperature  $28^{\circ}$  had no opportunity of overtaking  $23^{\circ}$ , as has been the case with  $13^{\circ}$  and  $17^{\circ}$ . But  $25\frac{1}{2}^{\circ}$  and  $23^{\circ}$  were practically equal on Sept. 1 and yet in  $5^{\circ}$  after preliminary treatment with  $23^{\circ}$  the length of the organs always surpasses their length in  $25\frac{1}{2}^{\circ}$ .

3. Between  $13^{\circ}$  and  $17^{\circ}$  there is no clear difference as far as the young leaves are concerned. On the whole it seems that after  $23^{\circ}$  a cooler after-treatment with  $13^{\circ}$  is to be preferred to  $17^{\circ}$ , and that the organs after  $25\frac{1}{2}^{\circ}$  and  $28^{\circ}$  and next  $13^{\circ}$  and  $17^{\circ}$  are longest in the 12 experiments, but that there is not much difference between these four kinds. Considering however that on Sept. 1, the organs in  $28^{\circ}$ , both leaflets and cluster lag a little behind in length with  $25\frac{1}{2}^{\circ}$  and  $23^{\circ}$ , we arrive at the conclusion, that  $28^{\circ}$  and next  $13^{\circ}$ , but especially  $17^{\circ}$  is most effectual. Here again it is proved, how important preliminary treatment in high temperature is, so that the organs, initially lagging behind in length in embryonic state make up for lost time most satisfactorily. It may be all but safely accepted that in those higher temperatures the number of embryonic cells is greater and the extension does not progress so fast as in the less high temperatures ( $20^{\circ}$ ,  $23^{\circ}$ ), so that later on there are more cells available for extension. I state this only as a supposition. In a later paper its correctness will be probed.

4. Judging from the cluster-length  $17^{\circ}$  is a little more advanced than  $13^{\circ}$ . Considering the mean error (above 0.40) no value must be attached to this in one group, but as it is repeated perfectly regularly three times (after  $23^{\circ}$ ,  $25\frac{1}{2}^{\circ}$ ,  $28^{\circ}$ ), we may attach value to it in my opinion.

TABLE 30. Order of succession of coming into bloom, the quickest being indicated 1, — etc. On April 19, 1924.

	$5^{\circ}$	$9^{\circ}$	$13^{\circ}$	$17^{\circ}$
$23^{\circ}$	3	3	2 to 3	2 to 3
$25\frac{1}{2}^{\circ}$	4	3	1	1
$28^{\circ}$	5	4	2	1 to 2

$25\frac{1}{2}^{\circ}$ — $13^{\circ}$  and  $25\frac{1}{2}^{\circ}$ — $17^{\circ}$  are *celerrimal* as to coming into bloom, next  $28^{\circ}$ ; the after-treatment in  $9^{\circ}$  and  $5^{\circ}$  causes distinct delay. It

strikes us again that the *after-treatment of 5° retards the less, according as the warm initial temperature was lower.*

TABLE 31. Number of assimilating leaves per 10 plants

	5°	9°	13°	17°
23°	37	36	37	37
25 1/2°	38	39	41	39
28°	40	39	40	40

It appears that especially the warm initial temperature is decisive, with respect to the growing out of all young leaflets, which are already there at the beginning of July; upon these the cool after-treatment has no perceptible influence, so that after the treatment with 5° the leaves extend as well as after 17°. Though 23° is not so very unfavourable, yet it is corroborated again, that already by that temperature some leaflets are arrested in growth. To make them all unfold it appears again that at least 25° is needed.

In connection with this we want to draw the attention to the increase in weight. We started with 12 groups, the average initial weight of which varied in the various groups from 12.1 to 12.8 grams per bulb in July 1923.

TABLE 32. Increase in weight per bulb from July 1923 to July 1924.

	5°	9°	13°	17°
23°	12.3	14.0	11.6	13.9
25 1/2°	12.8	14.6	21.8	18.7
28°	14.5	15.9	18.9	19.2

We know already that slight differences of weight cannot be attached much value to; but it is evident that in all cases 23° lags behind higher temperatures, that after 25 1/2° and 28° an after-treatment with 13° or 17° gives the greatest increase in weight. Conspicuously higher among these four is 25 1/2°—13°; whether this is of real value, I could not conclude from this one figure. I wish to point out that after treatment in 25 1/2° and 28°—13° and 17°

increases of weight are found, corresponding very well with those which were ascertained the year before (see table 8 part I), which are relatively high in comparison with the experiments of §§ 11, 12 and 13 made in the same year.

Let us now consider the flower-clusters which were of more moment in these experiments than the increase in weight.

TABLE 33. Number of *succeeded clusters* on 30 plants.

	5°	9°	13°	17°
23°	22	23	28	29
25½°	15	25	29	30
28°	14	26	28	29

It is obvious that after-treatment with 9° or 5° is injurious, but this criterion corroborates anew, that the disadvantage of 5° is the smaller according as the preliminary treatment was a little less warm (23°).

Between 13° and 17° there is no certain difference; at any rate 25½°—17° and 13° are among the optimal treatments.

TABLE 34. Number of flowers per succeeded cluster. The number from which the average is taken, we find in the above table 33.

	5°	9°	13°	17°
23°	7.27 ± 0.29	7.09 ± 0.29	7.43 ± 0.34	6.65 ± 0.26
25½°	7.47 ± 0.30	6.25 ± 0.27	6.54 ± 0.23	6.41 ± 0.29
28°	6.00 ± 0.37	5.85 ± 0.26	5.82 ± 0.24	5.72 ± 0.23

It is very probable, that there where many clusters don't develop in consequence of a less satisfactory treatment (5°), the strongest clusters with more flowers are most likely retained. Therefore I think it better to leave these numbers of flowers out of account. If we regard the remaining columns, especially 13° and 17°, it appears that with respect to the number of flowers exposure to 23°



seems to be more favourable and to  $28^{\circ}$  certainly is a little more unfavourable than  $25\frac{1}{2}^{\circ}$ . As on Sept. 1, when the cooler after-treatment begins, the number of flowers has already been fixed and consequently  $23^{\circ}$ — $13^{\circ}$  and  $17^{\circ}$  may be added up, it is obvious, that the advantage of  $23^{\circ}$  to  $25\frac{1}{2}^{\circ}$  with respect to number of flowers, if existing, is very slight. As for the rest for celerrimal flowering and especially for increase in weight  $25\frac{1}{2}^{\circ}$ — $17^{\circ}$  and  $13^{\circ}$  are certainly to be preferred, my opinion is that for an *optimal combination of optima* it is safest to abide by  $25\frac{1}{2}^{\circ}$  (practically  $24\frac{1}{2}^{\circ}$  to  $26\frac{1}{2}^{\circ}$ ) 8 weeks and  $4\frac{1}{2}$  weeks in  $17^{\circ}$  or a little lower (practically  $14^{\circ}$  to  $17^{\circ}$ ). On the influence of the temperatures on the extension of the organs after ca. Sept. 1, detailed experiments are being made by Miss LUYTEN and Miss VERSLUYS. It is desirable to await these results. Nor shall I give a summary of the results described in these §§, because after some time I shall be able to communicate other experiments which will enable us to form a final conclusion for the variety Queen of the Blues on the following 3 points: 1. celerrimal flowering (early-flowering), 2. optimal flowering or optimal field-culture, in which flowering and increase in weight are combined as well as possible, and 3. optimal increase in weight, in which the flowering is left out of account.

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**Chemistry.** — “*In-, mono- and plurivariant equilibria*”. XXVIII.

By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 25, 1924).

*Singular equilibria.*

In the previous communication we have seen that the “singular part” of an equilibrium determines a phases-reaction, in which not all phases of the equilibrium are participating; and reversally, that a phases-reaction, in which not all phases participate, defines a singular part.

We have called the composants, which participate in the phases-reaction, the singular ones and those who do not participate in the phases-reaction, the indifferent composants.

When we divide the equilibria according to the number of phases-reactions, which may occur in the equilibrium, then we can summarise the results of some of the previous communications in the following way.

*I. Equilibria with one phases-reaction.*

A. All phases participate in the phases-reaction.

We then have an equilibrium  $E(n, r)(r)$ ; it is monovariant; in a  $PT$ -diagram it is represented by a curve; in each point of this curve it is completely defined.

B. There is a singular part.

a. Consequently we have an equilibrium  $E(n, r)(r')$ ; the number of indifferent phases is  $R = r - r' > 0$ .

When we represent this equilibrium by  $E(N, R)$ , in which  $N$  is the number of indifferent composants, then it has  $N - R + 1$  freedoms; when all singular phases have a constant composition, then is  $N - R + 1 = n - r + 2$ . We may choose  $T$  or  $P$  as independent variables, but not both together.

It is represented in a  $PT$ -diagram by its singular  $PT$ -curve; in each part of this curve the singular part is completely defined, but the indifferent part has still  $N - R$  freedoms.

b. There is an accidentally singular part.

It is represented in a  $PT$ -diagram by the point of contact of its

singular  $PT$ -curve with the  $PT$ -curve of the equilibrium in its general form. Consequently  $T$  and  $P$  are completely defined.

## *II. Equilibria with two or more phases-reactions.*

To each phases-reaction belongs, therefore, a singular part. When  $q$  phases-reactions occur, so that there are also  $q$  singular parts, then we have represented it by  $E(n.r)S_q$ .

An equilibrium  $E(n.r)S_q$  is represented in a  $PT$ -diagram by the point of intersection  $i$  of its  $q$  singular  $PT$ -curves.

When there are more than two singular  $PT$ -curves, then the directions of those  $q$ -curves in point  $i$  are corresponding with one another<sup>1)</sup>.

Consequently  $P$  and  $T$  are completely defined yet the equilibrium may still have freedoms sometimes.

Now we shall apply those general considerations to some of the examples, which have been mentioned in the beginning of the previous communication. In the equilibrium *a* viz.

$$E(n.3)(2) = \text{solution} + (\text{ice} + \text{water vapour}) \quad . \quad . \quad (1)$$

the singular phases are placed again between parentheses, just as previously. The solution contains, besides water, still  $n-1$  other substances, which, however, following the supposition, are not volatile.

As only one phases-reaction is possible, in which not all phases participate, it belongs to the group *I. B.*; as the singular part is constant, it has  $n-3+2=n-1$  freedoms.

Consequently its singular  $PT$ -curve, by which it is represented in a  $PT$ -diagram is the sublimation-curve of the ice; viz. the curve, on which the inversion ice  $\rightleftharpoons$  water-vapour takes place. In each point of this curve the solution has still  $n-2$  freedoms.

The pressure  $P_x$  belonging to a temperature  $T_x$  of the equilibrium (1) is found therefore, from the known sublimation-curve of the ice; consequently this pressure  $P_x$  is the same for all equilibria (1), no matter how many and which substances the solution contains.

We may express this also in the following way: all equilibria (1) are represented in a  $PT$ -diagram by the same curve, how many and which substances the solution contains.

When we cool this system, then  $P$  and  $T$  change along the sublimation-curve of the ice. When anywhere on this curve a solid

<sup>1)</sup> Compare: F. A. H. SCHREINEMAKERS; these Proceedings 18, 1676.

substance  $A$  is separated, then (1) passes into:

$$E(n.4)(2) = A + \text{solution} + (\text{ice} + \text{watervapour}) \quad (2)$$

When at further cooling still a second substance is separated, then (2) passes into:

$$E(n.5)(2) = A + B + \text{solution} + (\text{ice} + \text{watervapour}) \quad (3)$$

etc. The same as above is valid for all those equilibria; consequently they are all represented by the sublimation-curve of the ice; each separation of a new phase diminishes however the number of freedoms with one.

When we cool the system so far that in a point  $i$  the number of the phases becomes  $n + 2$ , then arises an equilibrium:

$$E(n.n+2)S_3 = ((A + B \dots + \text{solution} + \text{ice} + \text{watervapour})) \quad (4)$$

wherein the double parentheses indicate, that more phases-reactions are possible between the phases, or in other words, that those phases form more singular parts. In this case there are three viz.:

$$(A + B \dots + \text{solution} + \text{ice}), (A + B \dots + \text{solution} + \text{watervapour})$$

and  $(\text{ice} + \text{watervapour})$

Consequently the equilibrium belongs to group II and it is invariant; it is represented in the  $PT$ -diagram by the point of intersection  $i$  of: the melting-curve of  $A + B \dots + \text{ice}$ , the evaporation-curve of  $A + B \dots + \text{solution}$  and the sublimation-curve of the ice.

When we cool the equilibrium (1), so that it passes at last into an equilibrium (4), then it proceeds the same  $PT$ -curve, therefore; consequently the formation of new phases causes no change of direction of its  $PT$ -curve.

When the equilibrium (1) passes into equilibrium (2) in a point  $r$  by cooling, then it is possible that the substance  $A$  gets accidentally such a composition that it becomes an equilibrium:

$$E(n.4)S_3 = ((A + \text{solution} + \text{ice} + \text{watervapour}))$$

with the three singular parts:

$$(A + \text{solution} + \text{ice}), (A + \text{solution} + \text{watervapour})$$

and  $(\text{ice} + \text{watervapour})$ .

The point  $r$  then is the point of intersection of the three singular  $PT$ -curves.  $T$  and  $P$  are completely defined then.

Similar considerations are valid also for equilibria as:

$$E(n.3)(2) = \text{solution} + (\text{solid benzene} + \text{vapour benzene}) \quad (5)$$

$$E(n.3)(2) = \text{solution} + (\text{solid naphtalene} + \text{vapour naphtalene}) \quad (6)$$



etc.; their singular  $PT$ -curves are the sublimation-curves of benzene, naphthalene etc.

An example of the equilibria, mentioned sub (h) we have f.i. in:  
 $E(n.4)(3) = \text{solution} + (Na_2SO_4 \cdot 10 H_2O + Na_2SO_4 + \text{watervapour})$  (7)

In a  $PT$ -diagram it is represented by the dehydration-curve of the  $Na_2SO_4 \cdot 10 H_2O$ , viz. by the  $PT$ -curve on which takes place the inversion:



In each point of this curve the solution still has  $n-3$  freedoms.

The vapour-tension  $P_x$  belonging to a temperature  $T_x$  is found, therefore, from the known dehydration-curve of the  $Na_2SO_4 \cdot 10 H_2O$ ; this pressure  $P_x$  is the same for all equilibria (7) how many and which substances the solution contains.

When, at decrease of temperature, still other phases are separated, then similar considerations as above are valid.

In the equilibrium:

$$E(n.3)(2) = \text{solution} + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad . \quad (8)$$

$F_\alpha$  and  $F_\beta$  are two modifications of a solid substance  $F$ . It is represented in the  $PT$ -diagram by the curve, on which the inversion  $F_\alpha \rightleftharpoons F_\beta$  takes place; we call this the modification-curve of  $F_\alpha + F_\beta$ . This equilibrium has  $n-1$  freedoms; consequently the solution has still  $n-2$  freedoms in each point of its  $PT$ -curve.

When we take f.i. two modifications of  $NH_4NO_3$ , then they can be in equilibrium with their aqueous solution at temperatures and under pressures, which belong to the modification-curve of those two nitrates. As  $n=2$ , at each temperature the composition of the solution is defined also.

When we add still a third substance, f.i. alcohol, aceton or  $NaCl$ , etc. then the solution has still one freedom in each point of the  $PT$ -curve; in a concentration-diagram it is represented then by a curve.

Independent on the number and the character of the substances, which occur in the solution, consequently to each temperature  $T_x$  belongs a definite pressure  $P_x$  which is defined by the modification-curve of  $F_\alpha + F_\beta$ .

When we take f.i.  $\alpha$ -rhombic and  $\beta$ -rhombic  $NH_4NO_3$ , then is, in accordance with TAMMANN f.i. for  $T_x = 32^\circ, 40^\circ$  and  $50^\circ$  the

pressure  $P_x = 1,252$  and  $550$  atmospheres; its termination point towards higher pressures is situated at  $T = 64^\circ,2$  and  $P = 930$  atmospheres.

Of course similar considerations are valid also for the equilibrium

$$E(n.3)(2) = \text{vapour} + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad (9)$$

Above we have said that an equilibrium is represented by its singular  $PT$ -curve; this does not involve that, reversally, each point of this curve represents a stable condition of this equilibrium. We have viz. seen already that the equilibrium (1) may be converted by cooling successively into (2), (3) etc. We shall discuss this more in detail with a definite example. For this we take the equilibrium (9) and we shall firstly suppose that it contains two components only (f.i. water and  $\text{NH}_4\text{NO}_3$ ; of this salt we take again the two modifications, like above); consequently we have:

$$E(2.3)(2) = \text{vapour} + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad (10)$$

The lowest pressure, under which this equilibrium may exist, is the pressure of the common sublimation-point of  $F_\alpha + F_\beta$ . This lowest finishing-point of the modification-curve of  $F_\alpha + F_\beta$  we call  $s$ . The pressure  $P_s$  shall differ practically extremely little from zero; the temperature  $T_s$  is very little lower than  $32^\circ$ .

We now press together the equilibrium (10), so that it proceeds along the modification-curve from  $s$  towards higher pressures; then in each point of this curve the composition of the vapour is completely defined. In a definite point  $i$  now as new phase a liquid is formed, so that occurs the equilibrium:

$$E(2.4) S_i = (\text{solution} + \text{vapour} + F_\alpha + F_\beta) \quad . \quad . \quad (11)$$

with the three singular parts:

$$(\text{solution} + \text{vapour} + F_\alpha) \quad , \quad (\text{solution} + \text{vapour} + F_\beta) \text{ and } (F_\alpha + F_\beta).$$

This equilibrium is invariant; the point  $i$  is the point of intersection of three singular  $PT$ -curves.  $T_i$  is somewhat lower than  $32^\circ$ ;  $P_i$  is smaller than  $35$  mM. Hg: the vapour-pressure of pure water.

By compressing further (11) is converted at  $T_i$  and under  $P_i$  into:

$$E(2.3)(2) = \text{solution} + (F_\alpha + F_\beta) \quad . \quad . \quad . \quad (12)$$

which remains at further increase of pressure, till anywhere in a point  $a$  of the modification-curve something else takes place.

The equilibria (10) and (12) are represented, therefore, both by the same curve; (10) is however stable only on the part  $si$  and (12)

on the part  $ia$ . They meet in the point  $i$ , where (11) occurs.

The phenomena become otherwise when the system contains more than two components (besides  $\text{NH}_4\text{NO}_3$  and water f.i. yet alcohol, acetone etc.). Instead of (10) and (12) we then have:

$$E(n.3)(2) = \text{vapour} + (F_\alpha + F_\beta) \quad (13)$$

$$E(n.3)(2) = \text{solution} + (F_\alpha + F_\beta) \quad (14)$$

which have  $n-1$  freedoms; vapour and liquid may have, therefore, still an infinite number of compositions.

We now take an equilibrium (13) of definite composition. When this equilibrium proceeds, starting from  $s$  the  $PT$ -curve, then in a point  $i$  again liquid is formed and consequently arises an equilibrium

$$E(n.4)(2) = \text{solution} + \text{vapour} + (F_\alpha + F_\beta) \quad (15)$$

which is not invariant, but has still  $n-2$  freedoms. Equilibrium (15) shall proceed now at further increase of pressure along the singular curve till in a point  $r$  the vapour disappears and an equilibrium (14) is formed. This remains at further increase of pressure till anywhere in a point  $a$  something else occurs.

Consequently equilibrium (13) exists on part  $si$ , (15) on part  $ir$  and (14) on part  $ra$  of its singular  $PT$ -curve.

We have started from an equilibrium (13) which had a definite composition; when we change this, then the points  $i$  and  $r$  fall also on another place of the curve. As (13) may have infinitely many compositions, there is, therefore, also an infinite number of points  $i$  and  $r$ .

These points  $i$  and  $r$  may also coincide to a single point  $q$ ; this is the case when (15) becomes accidentally an equilibrium

$$E(n.4)S_1 = (\text{solution} + \text{vapour} + F_\alpha + F_\beta) \quad (16)$$

Then the point  $q$  is the point of intersection of the modification-curve with the  $PT$ -curves of the two other singular parts:

$$E(n.3)(3) = \text{solution} + \text{vapour} + F_\alpha \quad (17)$$

$$E(n.3)(3) = \text{solution} + \text{vapour} + F_\beta \quad (18)$$

When  $F_\alpha$  en  $F_\beta$  contain several components, then the  $PT$ -curves of (17) and (18) have generally a maximum of temperature; then they intersect the modification-curve in general in 2 points  $q^1$ .

It appears, therefore, from those considerations that the area's of the equilibria (13), (14) and (15) shall partly cover one another on the singular  $PT$ -curve. This is also clear in the following way.

<sup>1)</sup> For ternary systems compare: F. A. H. SCHREINEMAKERS, these Proceedings 16, 1148 etc. (1914).

When we take away the solution from (15), then one of the equilibria (13) arises; when we take away the vapour, then one of the equilibria (14) arises. In connection with our considerations in the previous communication, that, which is said above, follows at once herefrom.

We may assume also that an equilibrium (15) proceeding along its singular  $PT$ -curve passes into an equilibrium:

$$E(n.4) S_1 = (\text{solution} + \text{vapour}) + (F_\alpha + F_\beta) \quad (19)$$

Of course this is possible only then, when the solid modifications are sufficiently volatile. As now two phases-reactions may occur, (19) belongs to group II. Consequently the equilibrium is represented by the point of intersection  $q$  of the modification-curve with the  $PT$ -curve of the equilibrium:

$$E(n.2) (2) = \text{solution} + \text{vapour} \quad (20)$$

Consequently  $T_q$  and  $P_q$  are completely defined.

We take again the equilibrium (14). When it proceeds along its  $PT$ -curve towards higher pressures, then in a point  $q$  of this curve the equilibrium:

$$E(n.4) S_1 = \text{solution} + ((F_\alpha + F_\beta + F_\gamma)) \quad (21)$$

may be formed. Herein the three singular phases represent modifications of the same substance  $F$ . We now have the three phases-reactions  $F_\alpha \rightleftharpoons F_\beta$ ,  $F_\alpha \rightleftharpoons F_\gamma$ ,  $F_\beta \rightleftharpoons F_\gamma$ ; the point  $q$  is, therefore, the point of intersection of the three modification-curves.

Although  $T_q$  and  $P_q$  are completely defined, therefore, the solution has yet still  $n-2$  freedoms. When it is a binary solution, then it is completely defined; when it contains more than two components, then it may have an infinite number of compositions.

Further it is apparent that  $T_q$  en  $P_q$  are defined only by the substance  $F$  and that they are dependent on the number and the art of the other substances, which occur in the solution.

A similar equilibrium might be realisable when one of the components is f. i.  $\text{NH}_4\text{NO}_3$ . In accordance with TAMMANN at a temperature of  $64^\circ,2$  and under a pressure of 930 atmospheres the three modifications:  $\alpha$ -rhombic,  $\beta$ -rhombic and rhomboëdric of  $\text{NH}_4\text{NO}_3$ , exist next to one another. Consequently the equilibrium (21) will be able to exist at  $T_q = 64^\circ,2$  and  $P_q = 930$  atmospheres, how many and which other substances the solution contains.

Similar considerations are valid when in (21) besides the solution still other indifferent phases are occurring.



We now take the ternary equilibria:

$$E(3.3)(2) = \text{liquid} + (\text{solid substance} + \text{liquid}). \quad (22)$$

$$E(3.3)(2) = \text{liquid} + (\text{mixed-crystal} + \text{liquid}). \quad (23)$$

$$E(3.3)(2) = \text{liquid} + (\text{solid substance} + \text{vapour}). \quad (24)$$

$$E(3.3)(2) = \text{liquid} + (\text{mixed-crystal} + \text{vapour}). \quad (25)$$

We here mean with „solid” substance a solid substance with constant composition. We now distinguish three cases.

a. The singular part contains also the three components.

This is always the case in the equilibria (22) and (23), wherein one of the singular phases is a liquid; in the equilibria (24) and (25) this can be the case only, when the three substances are volatile.

These equilibria belong to group *IB*; consequently they have  $N-R+1$  freedoms. As there is no indifferent component,  $N=0$ ; as there is one indifferent phase,  $R=1$ . Consequently the equilibria are invariant; temperature, pressure and composition of the phases are, therefore, completely defined.

In a *PT*-diagram they are represented by a definite point *q* of their singular *PT*-curve. In (22) this is the melting-curve, in (24) the sublimation-curve of the solid substance; in (23) it is the curve on which the conversion: mixed-crystal  $\rightleftharpoons$  liquid takes place; in (25) it is the curve on which the conversion: mixed-crystal  $\rightleftharpoons$  vapour takes place.

The point *q* is defined on the singular *PT*-curve by the fact that those equilibria belong to group *IBb*; consequently the point *q* is the point of contact of their singular *PT*-curve with the *PT*-curve of the annexed equilibrium in its general form. This is for the equilibrium (22):

$$E(3.3)(3) = \text{liquid} + \text{solid} + \text{liquid}. \quad (26)$$

consequently the ternary equilibrium of three phases, which have such composition, that one of them may proceed from the two other ones.

b. the singular part contains two components only.

Of course this may occur only in the equilibria (24) and (25); for this it is necessary that the component, which occurs only in the liquid, is not volatile. As  $N=1$  and  $R=1$ , those equilibria now have one freedom. Consequently they are represented in a *PT*-diagram by its singular *PT*-curve; in each point of this curve the composition of the phases is completely defined, therefore.

c. the singular part contains one component only.

This may occur only in the equilibrium (24). As  $N=2$  and  $R=1$ ,

this equilibrium has 2 freedoms. We now may, however, represent the number of freedoms also by  $n-r+2$ , as the two singular phases are constant; it then has  $3-3+2=2$  freedoms which is in accordance with  $N-R+1$ .

Consequently the equilibrium is represented in a  $PT$ -diagram by the sublimation-curve of its solid substance, in each point of this curve the liquid has still one freedom.

We assume that in the equilibrium:

$$E(n.3) = \text{liquid} + \text{solid substance} + \text{vapour} \quad . \quad . \quad (27)$$

all phases contain the  $n$  components. The equilibrium

$$E(n.3)(3) = \text{liquid} + \text{solid substance} + \text{vapour} \quad . \quad . \quad (28)$$

in which the three phases have such composition, that one of them can be composed from the two other ones, is, therefore, monovariant. Consequently it is represented in the  $PT$ -diagram by a curve.

Equilibrium (27) also may pass into one of the equilibria:

$$E(n.3)(2) = (\text{liquid} + \text{solid substance}) + \text{vapour} \quad . \quad . \quad (29)$$

$$E(n.3)(2) = \text{liquid} + (\text{solid substance} + \text{vapour}) \quad . \quad . \quad (30)$$

$$E(n.3)(2) = \text{solid substance} + (\text{liquid} + \text{vapour}) \quad . \quad . \quad (31)$$

Each of those equilibria has  $N-R+1$  freedoms. Each is represented, therefore, by a definite point of its singular  $PT$ -curve. Consequently equilibrium (29) is situated in a point  $q$  of the melting-curve of the solid substance, equilibrium (30) in a point  $r$  of the sublimation-curve of the solid substance and equilibrium (31) in a point  $s$  of the  $PT$ -curve, on which the conversion: liquid  $\rightleftharpoons$  vapour takes place.

Each of those three equilibria belongs to group  $IBb$ ; to each belongs viz. a definite equilibrium in its general form. In this definite case this equilibrium in its general form is the same for the three equilibria, viz. equilibrium (28).

The points  $q$   $r$  and  $s$  are situated, therefore, on the  $PT$ -curve of equilibrium (28) and they are the points of contact of this curve with the singular  $PT$ -curves of the equilibria (29), (30) and (31).

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*To be continued.*

**Mathematics.** — “*Ueber die Wahrscheinlichkeit dass zwei natürliche Zahlen relativ prim sind.*” Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of November 29, 1924).

Es seien  $M$ ,  $A \leq M$  und  $B \leq M$  natürliche Zahlen  $> 1$ .  $A$  und  $B$  sind dann und nur dann nicht relativ prim:  $(A, B) \neq 1$ , wenn  $A$  und  $B$  durch wenigstens eine Primzahl  $p \leq M$  teilbar sind. Wir nennen  $\sigma(M)$  die Anzahl der Paare  $A, B$  mit  $(A, B) \neq 1$ .

Diese Anzahl berechnen wir folgendermassen. Sei  $B$  fest und seien  $p_1, p_2, \dots$  die unter einander verschiedenen Primfactoren von  $B$ . Dann ist die Anzahl der Zahlen  $A$ ,  $1 < A \leq M$ , die durch  $p_i$  teilbar sind, gegeben durch  $\left[ \frac{M}{p_i} \right]$ ; also ist die Anzahl der Zahlen  $A$ , wofür  $(A, B) = \text{einem } p_i^{h_i} \ (h_i \geq 1)$ , ist:  $\sum_{p_i} \left[ \frac{M}{p_i} \right]$ . Daher die Anzahl

der Zahlen  $A$ , wofür  $(A, B) = \text{einem } p_i^{h_i}$  oder  $= \text{einem } p_i^{h_i} \cdot p_k^{h_k} \ (i \neq k)$  ist, gegeben durch

$$\sum_{p_i \leq M} \left[ \frac{M}{p_i} \right] - \sum_{\substack{p_i < p_k \\ p_i p_k \leq M}} \left[ \frac{M}{p_i p_k} \right].$$

Durch Induktion findet man auf diese Weise die Anzahl  $v(B)$  der Zahlen  $A \leq M$  mit  $(A, B) \neq 1$  ausgedrückt durch <sup>1)</sup>:

$$v(B) = \sum \left[ \frac{M}{p_i} \right] - \sum_{p_i < p_k} \left[ \frac{M}{p_i p_k} \right] + \sum_{p_i < p_k < p_l} \left[ \frac{M}{p_i p_k p_l} \right] - \dots \quad (1)$$

Da nun

$$\sigma(M) = \sum_{B=2}^{B=M} v(B) \dots \dots \dots (2)$$

ist, finden wir

$$\sigma(M) = \sum_{B=2}^{B=M} \left( \sum_{p_i} \left[ \frac{M}{p_i} \right] \right) - \sum_{B=2}^{B=M} \left( \sum_{p_i < p_k} \left[ \frac{M}{p_i p_k} \right] \right) + \dots \quad (3)$$

<sup>1)</sup> Verg. E. LANDAU, Handbuch . . . Primzahlen, I, S. 67. Leipzig (1909).

Ordnen wir hier in jeder Doppelsumme die Glieder nach den verschiedenen Primzahlen  $p, q, \dots$ , die  $\leq M$  sind und nennen  $B, A$  nicht verschieden von  $A, B$  (denn  $(A, B) = 1$  und  $(B, A) = 1$  drücken dasselbe aus), so bekommen wir:

$$2\sigma(M) = \sum_{p \leq M} \left[ \frac{M}{p} \right] \left( \left[ \frac{M}{p} \right] + 1 \right) - \sum_{p < q \leq M} \left[ \frac{M}{pq} \right] \left( \left[ \frac{M}{pq} \right] + 1 \right) + \dots \quad (4)$$

Hieraus finden wir die Anzahl  $\tau(M)$  von Zahlenpaaren  $A, B, A \leq M, B \leq M$ , wofür  $(A, B) = 1$  ist:

$$\tau(M) = \frac{1}{2} M(M+1) - \sigma(M) \quad . \quad . \quad . \quad (5)$$

Daher ist die Wahrscheinlichkeit, dass unter diesen Bedingungen  $(A, B) = 1$  wird:

$$w(M) = 1 - \frac{1}{M(M+1)} \left\{ \sum_p \left[ \frac{M}{p} \right] \left( \left[ \frac{M}{p} \right] + 1 \right) - \sum_{p < q} \left[ \frac{M}{pq} \right] \left( \left[ \frac{M}{pq} \right] + 1 \right) + \dots \right\} \quad (6)$$

Nun nehmen wir  $M \rightarrow \infty$  und zeigen, dass  $w(\infty)$  existiert und  $= 0,607 \dots$  ist.

Hiezu beweisen wir erstens, dass die Reihe

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \dots \quad (7)$$

der positiven Zahlen

$$\sigma_n = \sum_{2 \leq p_1 < \dots < p_n} \frac{1}{(p_1 p_2 \dots p_n)^2} \quad . \quad . \quad . \quad (8)$$

konvergiert. Dabei sind  $p_1, p_2, \dots, p_n$   $n$  verschiedene Primzahlen.

Wenn wir in der absolut und deshalb auch unbedingt konvergenten Reihe (8) nacheinander die Faktoren  $\frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{5^2}, \dots$  absondern, erhalten wir:

$$\begin{aligned} \sigma_n &= \frac{1}{4} \cdot \sum_{3 \leq p_1 < \dots < p_{n-1}} \frac{1}{(p_1 p_2 \dots p_{n-1})^2} + \frac{1}{9} \cdot \sum_{5 \leq p_1 < \dots < p_{n-1}} \frac{1}{(p_1 p_2 \dots p_{n-1})^2} + \dots \\ &< \left( \frac{1}{4} + \frac{1}{9} + \frac{1}{25} + \dots \right) \cdot \sum_{3 \leq p_1 < \dots < p_{n-1}} \frac{1}{(p_1 p_2 \dots p_{n-1})^2} \\ &< \left( \sum_{p=2}^{\infty} \frac{1}{p^2} \right) \cdot \sigma_{n-1} < \left( \sum_{n=2}^{\infty} \frac{1}{n^2} \right) \cdot \sigma_{n-1} = (\zeta(2) - 1) \cdot \sigma_{n-1}, \end{aligned}$$



also

$$\sigma_n < k\sigma_{n-1}, \quad k = \zeta(2) - 1 = 0,6449 \dots < 1 \quad \dots \quad (9)$$

Daher ist die Reihe (7) konvergent.

Nun betrachten wir die für jedes  $x \geq 2$  und  $n = 1, 2, \dots$  definierte Funktion

$$f_n(x) = \frac{1}{x(x+1)} \cdot \sum_{\substack{2 \leq p_1 < \dots < p_n \\ p_1 p_2 \dots p_n \leq x}} \left[ \frac{x}{p_1 p_2 \dots p_n} \right] \left[ \frac{x}{p_1 p_2 \dots p_n} + 1 \right] \quad (10)$$

$f_n(x)$  ist für alle  $x$  beschränkt, denn wir haben:

$$\begin{aligned} f_n(x) &\leq \frac{1}{x(x+1)} \cdot \sum_{\substack{2 \leq p_1 < \dots < p_n \\ p_1 p_2 \dots p_n \leq x}} \frac{x}{p_1 p_2 \dots p_n} \cdot \frac{x + p_1 p_2 \dots p_n}{p_1 p_2 \dots p_n} \\ &< \frac{1}{x(x+1)} \cdot \sum_{\substack{2 \leq p_1 < \dots < p_n \\ p_1 p_2 \dots p_n \leq x}} \frac{x}{p_1 p_2 \dots p_n} \cdot \frac{x + x}{p_1 p_2 \dots p_n}, \\ f_n(x) &< 2 \sigma_n \quad \dots \quad (11) \end{aligned}$$

Nach dem sogenannten Kriterium von WEIERSTRASS<sup>1)</sup> ist daher  $f_1(x) + f_2(x) + \dots$  und daher umsomehr auch  $f_1(x) - f_2(x) + \dots$  für alle  $x \geq 2$  gleichmässig konvergent und wir können in (6) gliedweise zur Grenze  $M \rightarrow \infty$  übergehen. Wegen

$$\lim_{M \rightarrow \infty} \frac{1}{M(M+1)} \cdot \left[ \frac{M}{a} \right] \left[ \frac{M}{a} + 1 \right] = \frac{1}{a^2}$$

erhalten wir:

$$\begin{aligned} w = \lim w(M) &= 1 - \sum \frac{1}{p^2} + \sum \frac{1}{p^2 q^2} - \dots \\ &= \left(1 - \frac{1}{2^2}\right) \left(1 - \frac{1}{3^2}\right) \dots = \frac{1}{\zeta(2)}, \end{aligned}$$

somit

$$w = 0,607 \dots \quad \dots \quad (12)$$

<sup>1)</sup> Vgl. z.B. K. KNOPP, Theorie und Anwendung der unendlichen Reihen, Springer (1922), S. 332.

**Histology.** — "*Tactile corpuscles and protopathic sensibility of the skin in a case of nerve-regeneration*". By Prof. J. BOEKE and Dr. G. C. HERINGA.

(Communicated at the meeting of September 27, 1924).

Next to our higher sense-organs it is especially the skin, which by its complex sensibility brings us into continual contact with the world around us. The most different kinds of stimuli, differences in temperature, heat and cold, light touch and acute pain will be perceived by the skin with a startling discriminating power, provided only that the stimuli reach the different kinds of tactile corpuscles or sensory nerve-endings, distributed throughout the skin and the underlying tissues. And since the discoveries by HERZEN and BLIX, we not only know, that these different stimuli represent independent units, which give rise to entirely independent sensations, that even the perception of heat and cold are of a different nature and may be destroyed independently of each other, but we know too, that these different sensations are not appreciated by the skin diffusely, but that the different forms of sensation possessed by the skin are due to the existence of small areas ("spots") of specific sensibility. By suitable methods spots can be demonstrated in the normal skin where cold alone can be appreciated (cold spots, BLIX 1882). Analogous spots, more sparsely scattered, can be shown to be devoted entirely to sensations of heat. There are spots peculiarly sensitive to the prick of a sharp needle. Between these spots the skin is not sensitive to the same stimuli, which gave a distinct sensation when applied to the spots, provided only we take care to apply a stimulus weak enough not to cause radiation of the stimulus to adjacent sensitive spots, or to stimulate the deeper lying tissues.

The distribution of these different spots in a given piece of skin is of a constant nature. A "cold spot" in a normal piece of skin remains a cold spot indefinitely, but in different persons they are not always found in exactly the same places, although their general distribution, their density in a given area of the skin, their general arrangement is the same, when studied in different persons of normal health.

As is well known, anatomical investigation has revealed in the skin and the underlying tissues (subcutaneous tissue, fasciae, tendons, joints) quite a number of different sense-organs, varying in form, arrangement and distribution in the various parts of the body. When we confine ourselves to the common normal skin, and do not take into consideration those parts of the skin peculiarly adapted to the perception of special sensations (point of the tongue, organ of EIMER, cornea of conjunctiva bulbi, glans penis, clitoris, nipple, etc.), we may distinguish the following forms of afferent nerve-endings in the skin and the underlying tissues:

*a. epidermis:*

1. free-ending terminal ramifications of the afferent nerves running between the cells<sup>1)</sup> of the epithelium.

2. tactile discs of RANVIER and intraepithelial expansions of DOGIEL (paniers intraépithéliaux, expansions hédériformes), flattened disc- or leaflike enlargements of the nerve-fibres, lying between cells of the deeper layers of the epithelium and in close connection<sup>1)</sup> with special enlarged epithelium cells.

3. small arborisations of terminal nerve-fibres lying close against the basal side of the epithelium ("terminaisons arboriformes" of DOGIEL).

*b. corium.*

4. different forms of tactile corpuscles of WAGNER-MEISSNER in the papillae of the corium.

5. free-ending terminal arborisations (touffes papillaires, flocculi, pelotons libres), in the connective tissue of the papillae.

6. corpuscles of GOLGI-MAZZONI, strongly branched and curved terminal arborisations, the ends often appearing as flattened expansions, often concatenated, and lying in a core, surrounded by a lamellated connective-tissue capsule, in the corium and the adjacent layers of the subcutaneous tissue.

7. corpuscles of RUFFINI, terminal arborisations, lying in the interstices of small interwoven bundles of connective tissue, sometimes closely built, sometimes larger; they are mostly found in the subcutaneous tissue, and are not enclosed by a capsule. In the corium they are rare.

*c. subcutaneous tissue.*

8. intermediate forms between the corpuscles of GOLGI-MAZZONI and the following.

9. corpuscles of VATER-PICINI. Tactile bodies of an oval shape and

<sup>1)</sup> See J. BOEKE. BRAIN, Vol. 44. Page 21. 1921 and *Zeitschr. f. mikr. Anatom. Forschung*, Bd. 2. 1925.

a large size, and containing a core, in the middle of which runs the central nerve-fibre, and which is surrounded by numerous concentric membranous tunics, encasing each other like the coats of an onion.

When we add to these terminal corpuscles the delicate nerveplexus in the corium, described especially by RUFFINI, consisting of fine non-medullated fibres, the plexus of very fine amedullated nerve fibrils surrounding the different terminal corpuscles ("appareil de TIMOFFEEFF, bouquets de DOGIEL"), and the number of different forms presented for example by the corpuscles of MEISSNER, it is quite evident that the skin is endowed with such a variety of sensitive endorgans of different forms and aspects, that they may be held responsible for every kind of sensory perception of a particular quality, distinguishable by physiological investigation.

So it is quite natural, that again and again histologists have tried to establish a relation between the perception of different sensations and the stimulating of different kinds of sensory nerve-endings. But generally these essays have not met with a definite success, and at present we do not know, whether or not the different kinds of sensory nerve-endings react each of them on a particular kind of sensitive stimulus.

It is true, that the different kinds of sensory endorgans are found in larger numbers and more densely distributed there where the skin presents a higher developed sensitiveness and the cold spots, the heat spots, the pain spots, are more crowded, that for example especially the finger-tops are provided with a number of Pacinian and MEISSNER corpuscles, but even there where the different sensory spots are found lying close together, there is no distinct relation between the distribution of those spots and that of the different forms of sensory nerve endorgans, so that a particular kind of nerve-ending could be held responsible for a particular sensation.

The only way, in which this relation can be investigated, is the anatomical study of the nerve endorgans in cases of nerve regeneration, viz. in cases, where only one particular form of sensation is reestablished after the cutting of the nerve and the degeneration of all the different forms of sensory nerve-endings.

This not being done yet, it is quite natural, that physiologists and neurologists on the whole have left the relation between the anatomical endorgans and the different kinds of sensory perceptions for what it was, and have restricted themselves to the study of the physiological side of the question only.

A consequence of this way of studying these questions is the



sensory theory of H. HEAD, „the afferent nervous system from a new aspect”.<sup>1)</sup>

It being known, as was mentioned above, that during regeneration of the sensory nerves after section of the afferent nerves the perception of the different qualities of sensation does not return at the same time and in the same strength, it is obvious, that this provides us with a way to study the relations between the anatomical recovery of the nerves and nerve-endings during the regeneration of the nerve and the different qualities of returning sensation, provided only that the patient is a trained observer and the injury is determined beforehand. To fulfil those demands one of the cutaneous nerves of the left arm of HEAD himself was divided in the neighbourhood of his elbow, the ends were united again with silk sutures. Before this operation the sensory condition of the arm and back of the hand had been minutely examined, and the same was done during the regeneration process as accurately as possible.

The mode of recovery of sensation after this injury brought HEAD to the conclusion, that there are different forms of sensibility depending upon separate systems of nerves and nerve-endings in the peripheral nerves, viz. 1°. the *protopathic nerves*, sympathetic nerve-fibres, providing us with that curious dumb, undetermined, not exactly localised sensibility, which returns during the first phases of recovery after the cutting of the nerve, 2°. those nerves, which are more directly associated with motor impulses and pressure, and govern the *deep* sensibility, and 3°. those nerve-fibres, which end only in the superficial tissues, which are connected with the different forms of endorgans described above, and which give us the sharply defined, exactly localised sensibility to light touch, temperature and pain, the *epicritic nerves*. According to HEAD, these regenerate more slowly than the *protopathic nerve fibres*.

This theory may be characterized by the following quotations from the publications of HEAD and his collaborators:

“The whole body within and without is supplied by the *protopathic* system. The fibres of this system in the skin may be spoken of as somatic, those to the internal organs as visceral *protopathic* fibres. Thus we shall no longer speak of the afferent sympathetic system, but of the *protopathic* supply of the internal organs.

Another set of afferent fibres peculiarly associated with impulse of movement and pressure exists in connection with the Pacinian

<sup>1)</sup> H. HEAD, W. H. R. RIVERS and J. SHERREN. The afferent nervous system from a new aspect. BRAIN. Vol. 28. 1905.

organs. In the body and limbs an analogous system is found peculiarly susceptible to pressure, to the localisation of movement, and to the appreciation of position. The fibres of this system run in conjunction with the motor nerves.

In addition to these two systems, which are distributed to all parts of the body within and without, the surface of the body only is supplied by a third system, which we have called *epicritic*. This endows the skin with sensibility to light touch. To the impulses conducted by this system we owe the power of localizing the position of cutaneous stimuli, of discerning the doubleness of two points, and of discriminating between minor degrees of heat and cold, and other special attributes of sensation. The fibres of this system are more easily injured, and regenerate more slowly than those of the protopathic system. They are evidently more highly developed, and approach more nearly, to the motor fibres that supply voluntary muscle, in the time required for their regeneration." (Brain, Vol. 28, page 114).

In the following quotations too this view is sharply formulated:

"The afferent fibres in the peripheral nerves can be divided into three systems. 1. Those which subserve deep sensibility and conduct the impulse produced by pressure. The fibres of this system run mainly with the motor nerves, and are not destroyed by division of all the sensory nerves to the skin.

2. Those which subserve protopathic sensibility. This system of fibres and endorgans responds to painful cutaneous stimuli, and to the extremes of heat and cold. It also endows the hairs with the power of reacting to painful stimulation. These fibres regenerate rapidly after the ends of the nerve have been reunited; if the operation has been successfully performed, sensation begins to return within from seven to ten weeks. In any peripheral nerve the distribution of the protopathic fibres usually overlaps greatly the area supplied by the fibres of the adjacent nerves.

3. Those which subserve epicritic sensibility. The nerve fibres and endorgans of this system endow the part with the power of responding to light touch with a well-localised sensation. The existence of this system enables us to discriminate two points and to appreciate the finer grades of temperature called cool and warm. These fibres regenerate more slowly than those which subserve protopathic sensibility after reunion of a divided nerve, and sensation does not usually begin to return in less than six months under the most favourable conditions. The distribution of these fibres in the larger peripheral nerves, such as the median and ulnar, overlaps little

compared with the great overlapping of the protopathic supply". (Brain, Vol. 28, pag. 298). "What we have called "protopathic" and "epicritic" sensibility depend on two anatomically separate systems of fibres and endorgans". (Brain, Vol. 28, pag. 291).

In the entire litterature on the sensibility of the skin and its recovery after section of the nerve following on these publications we find this theory in discussion, either accepted or rejected.<sup>1)</sup> In recent years clinical neurologists do not seem to be inclined favourably towards it.

An anatomical investigation however of the regenerating endorgans themselves and a study of their histological features during the recovery of sensibility has not followed on the publication of the physiological basis of the theory. And after all that is what we need, for without a solid anatomical basis the physiological theory must needs remain a castle floating in the air.

This gap we will try to fill up. In March 1923 one of us (Dr. H.) slipped, fell into a window pane and cut his right wrist so, that the entire nervus ulnaris, the ulnar artery and the tendons of the ulnar muscles of the hand were severed below the wrist. Within an hour after the injury the tendons and the nerve were sutured, and the wound healed by first intention.

Both the ramus volaris superficialis and profundus and the ramus dorsalis of the ulnar nerve were entirely severed. Investigation showed that after the injury the entire area innervated by the ulnar nerve was absolutely insensitive to light touch, pain and temperature, and the muscles of the ulnar side of the hand including the m. adductor pollicis were paralysed (investigated by Dr. STENVERS).

When after a lapse of several months sensation began to return (see the following pages), Dr. STENVERS, neurologist, had the kindness to investigate with the utmost care the sensibility of the affected area and to map out the results carefully. After that just in the centre of the affected area, on the borderline between the palm and the hair-covered back of the hand, (fig. 1) a piece of the skin and underlying tissues was cut out (December 1923), fixed in neutralised solution of formaline, and afterwards<sup>2)</sup> stained after the BIELSCHOWSKY-method and cut into serial sections of 15—20  $\mu$  thickness. The

<sup>1)</sup> It was rejected for ex. in recent years by J. D. BORING (1916), LEWIS L. POLLOCK (1920), FRASIER and SILBERT (1920).

<sup>2)</sup> The results of impregnation being better after a prolonged sojourn of the tissues in neutralised formaline, the piece was impregnated and cut into sections in June 1924, after they had been in the formol-solution for about 6 months.



impregnation was perfect, and so a thorough histological examination of the sensitive endorgans and their behaviour during regeneration was possible.



Fig. 1.

Hand with paralysis of the ulnar nerve. Piece of skin cut out surrounded by a line.

The study of the *sensibility* of the injured area by Dr. STENVERS showed, that there was to be found a *typical protopathic sensibility*. Light touch (cotton-wool) was barely appreciated or not at all, stroking the hairs was appreciated very faintly, a light prick of a pin was entirely unappreciated, a strong prick often was only discriminated after a prolonged latent period (1 minute) and then gave rise to radiating paraesthesies, followed slowly by a somewhat better localised sensation of pain. Often, and more specially in the area, where afterwards the piece of skin was excised, a strong prick with a pin was not appreciated as pain, but only as touch, so that the patient thought that the knob of the pin was used, and not the sharp point. Localisation was very weak, and the distance at which two points of the compass could be discriminated was about 6 c.m., against about 5 m.m. in the identical spots on the normal hand. A renewed investigation some weeks ago ( $\pm 8$  months after the excision of the piece of skin) showed, that in the normal hand this distance had remained as it was (5 m.m.), but that on the skin surrounding the cicatrice the distance at which two points of the compass could be discriminated now had shortened to  $\pm 13$  m.m.

As to the sensibility to changes of temperature, according to the protocols of Dr. STENVERS, minor degrees of temperature produced no effect upon consciousness. Ice and warm water were appreciated,



the limits between which "hot" and "cold" were appreciated, were somewhat narrower than those given by HEAD for the typical protopathic sensibility. Minor differences of temperature (cool and warm) were not discriminated (Dec. 1923 and January 1924); in the area, from where the piece of skin was taken, water below  $21^{\circ}$  usually gave the sensation of "cold", water above  $38^{\circ}$  C. of "warm". On the spot, where the piece of skin was excised afterwards, water of  $18^{\circ}$  C. was appreciated either as "cold" or as "warm" with a latent period of about 4 seconds. When temperatures of  $5^{\circ}$  C. and of  $24^{\circ}$  C. were used as contrast,  $24^{\circ}$  C. was felt as "warm". A sensation of "cool" could not be produced, as it was possible in the normal hand.

Characteristic for the protopathic sensibility was the curious phenomenon, that a prick of a pin was not felt, but when such a prick all at once produced a sensation, it gave rise to an extremely unpleasant sensation, radiating widely over the affected area, and causing the patient to suddenly withdraw his hand. This corresponds exactly with the description of HEAD "closer examination of parts in this condition (viz. protopathic sensibility) shows that, although the hand has become sensitive to pain and to temperature, this sensibility is strangely altered. A prick is appreciated, but produces a sensation that radiates widely over the affected area. It causes unnatural discomfort, and the patient has an uncontrollable desire to withdraw his hand". (HEAD l. c. p. 101).

The *histological* investigation of the sections of the excised piece of skin gave the following results:

Regeneration of the nerves appeared to be in full swing. Nearly all the branches of the cutaneous nerves, visible in the sections, were filled with regenerating nerve fibres, not only the larger branches in the deeper layers of the connective tissue, but even the smaller and smallest branches in the superficial layers of the corium. As far as it could be determined, all these nerve fibres presented the typical regeneration phase of the protoplasmic bands of BÜNGNER, filled with a number of delicate neurofibrillar strands. Myelinsheaths did not seem to be developed yet.

Sympathetic nerve fibres too were present again. Everywhere alongside the bloodvessels delicate nerve fibres were to be found, and even around the walls of the sweat-glands and their ducts delicate nerve fibrillae could be seen, which here and there seemed to be in connection with the gland-cells.

But not only were the regenerating nerve fibres visible in the

branches of the cutaneous and subcutaneous nerve plexus, so that even the finest subepithelial nerve threads showed the regenerating neurofibrillae. The sensitive endorgans themselves were in full process of regeneration. Everywhere the delicate blackstained neurofibrillar strands could be seen entering the different endorgans, branching and dividing, forming small networks and loops (fig. 2, 3) and running in different directions through the conductive tissue of the sensitive corpuscles.



Fig. 2.

Papilla of the corium with a corpuscle of MEISSNER (*m*) with regenerating nerve fibres. *bl* = bloodvessels of papilla.

It is here not the right place, to describe this regeneration process in full detail. The general result of the histological examination of the sections was, that everywhere in the different endorgans regenerating nerve-fibres were to be found. But not in all. Among the tactile corpuscles of MEISSNER, which were found occurring in greater abundancy than is generally recorded for this part of the skin, some were still entirely devoid of regenerating nerve-fibres, others were already provided with new regenerated nerve-fibres (fig. 2). The endorgans of RUFFINI and of GOLGI-MAZZONI, which could be recognized as such in the sections, were all found provided with regenerating neurofibrillar strands. In fig. 3 is drawn a cross section through a corpuscle of RUFFINI, lying close to the corium in the subcutis, in full regeneration, which affords a striking example of the mode of regeneration of these endorgans.

Inside the epithelium itself regenerating nerve-fibres could only be traced in a few places. Whether there were more present, than those impregnated in the preparations, we should be inclined to doubt after what other preparations showed us. And whether

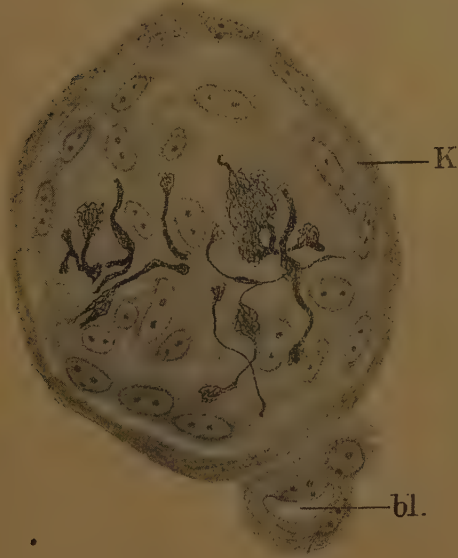


Fig. 3.

Cross section of a corpuscle of RUFFINI in regeneration. *k* = capsule.

this rare occurrence of intraepithelial nerve-fibres is accounted for by their not yet being regenerated, even this seems to us to be doubtful. For outside the classical areas of the skin, where the intraepithelial nerve-fibres are investigated by preference (finger-tips, snout of the pig or of the cow, organ of EIMER in the mole, taste-buds and their surroundings on the tongue, etc.), free-ending nerve-fibres in the epidermis seem to be very rare even in normal tissues. But as we are not yet able to compare our sections with normal material, taken from exactly the same spot on the normal left hand <sup>1)</sup>, this must remain only a supposition,

based however on the examination of a large number of sections of different parts of the skin.

Beside that of the tactile organs, the innervation of the hairs is coming back too. But here too the regenerating nerve-fibres present the same aspect as in the other sensitive endorgans, viz. an irregular plexiform arrangement of the neurofibrillar strands (fig. 4) in the root-sheath, entirely unlike the rather regular arrangement of the terminal arborisations of the nerve-fibres of the normal hair. Only in a few cases the regenerated nerve-fibres already presented a more regular arrangement, similar to that of normal hair-follicles.

In fig. 4 is drawn a longitudinal section through the outer part of the root-sheath of one of the hairs, that gives a clear picture of the irregular plexiform arrangement of the regenerating nerve-fibres.

<sup>1)</sup> A piece of normal skin, excised in the analogous spot from the normal left hand of Dr. H., was not yet ready for examination. In a second paper we hope to be able to be more exact.

In short, we find everywhere the nerve-fibres of the injured part of the skin in full process of regeneration.

This result is not favourable for the theory of HEAD.

For when we examine accurately the regenerating nerve-fibres in the different sensitive endorgans, their appearance, their ramifications, endloops and numerous flattened expansions, consisting of a fine

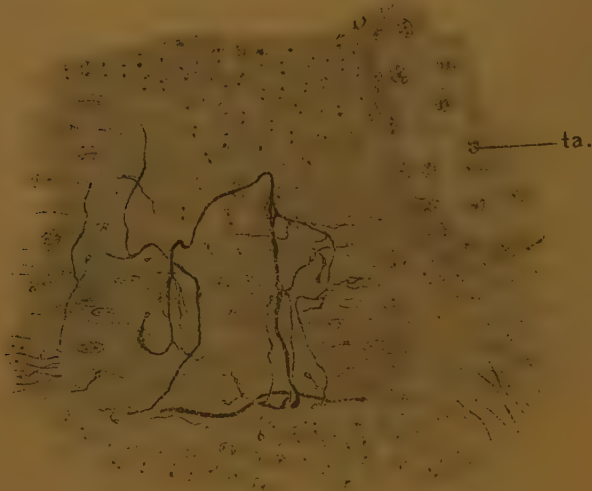


Fig. 4.

Longitudinal section through the outer part of the root-sheath of a hair with regenerating nerve-fibres. *ta* = sebaceous gland.

network of neurofibrillae, showing here and there a distinct connection with the protoplasm of the surrounding tactile cells (periterminal network), we can hardly doubt that a distinct sensory function, be it not yet a complete one, is exerted already by these endorgans.

And then, this being the case, it seems to be much more in harmony with what we know about the clinical and physiological features of regeneration to hold these regenerating sensory endorgans responsible for the curious dumb, diffused, widespread radiating sensation, unaccompanied by any definite appreciation of the locality of the spot stimulated, the *protopathic* sensibility of HEAD, then the sympathetic protopathic nerves of HEAD, of which the existence and the connection with the sensory end-organs has not been demonstrated anatomically and is based only on physiological considerations.

So to our opinion protopathic sensibility is due to the stimulation of sensory endorgans and corpuscles, which are still in process of



regeneration, the identical endorgans producing epicritic sensibility when they are completely restored to their normal conditions:

The curious radiating widespread unlocalised sensation may perhaps be due to the fact, that during this stage of regeneration no isolating myelin-sheaths are developed yet. All the regenerating nerve-fibres were still running inside the protoplasmic bands of BÜNGNER. As a rule myelin-sheaths, especially in the neighbourhood of the terminal organs, make their appearance only in the last stage of the regeneration-process.

In connection with these statements we should like to call the attention to what is known about the regeneration of motor nerve-endings<sup>1)</sup>. Here too we see that the first connection of the regenerating nerve-fibres with the muscle-fibres is formed by endorgans of the most bizarre and complicated structure, different from the normal motor-endings of which they are the substitutes.

In this stage of recovery motility is restored, but only in a weak und uncoordinated form. When we keep the animal alive some months after this functional activity is restored, we find the regenerating motor-endings again changing their form and we see everywhere reappear the normal form of the nerve-endings, characteristic for the species studied. Only then the normal motility is established again.

As there was no *absolute absence* of perception of sensations of a particular quality present, which corresponds with the fact, that in all sorts of endorgans regenerating nerve-fibres could be found, we were not able to establish the relation between the different forms of endorgans and the different sensations. This will only be possible after a careful *histological* investigation of a number of regeneration-cases, in which only the perception of a particular sensation is restored.

*Utrecht, September 1924.*

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<sup>1)</sup> J. BOEKE. Studien zur Nervenregeneration I, II. Verhandelingen der Kon. Akademie v. Wetensch. Deel XVIII 1916, 1917.

**Anatomy.** — "*Regarding the Influence of Domestication on the Structure of the Brain.*" By Dr. H. A. VERMEULEN. (Communicated by Prof. C. WINKLER.)

(Communicated at the meeting of October 25, 1924).

In an article in the *Bibliotheca genetica* of 1921, entitled "*Studien zum Domestikationsproblem. Untersuchungen am Hirn*", KLATT has recorded the results of his comparative study of a large variety of brains from dogs, wolves, and jackals. The selection of such material for comparison should be made with due caution. In domestic dogs the racial characteristics have considerable influence upon the shape, the volume, and the extent of the skull, consequently also on its contents: on the shape, and above all on the weight of the brain. The brain of an adult watchdog reaches about half the weight of the brain of a St. Bernard-dog of five months, if the body weight of the two animals is about the same. Age, nutritious conditions and sex should also be taken into account. At an advanced age the weight of the brain diminishes: a condition of excessive nutrition, so characteristic of the domestic dog, does not exist in his undomesticated ancestors; *ceteris paribus* the brain of female individuals weigh less than those of males. So for his research KLATT had to select dogs, which in all these relations came as near as possible to the wolf or the jackal. The fluid used as a fixing agent is also of great importance. Experience has taught us that formalin increases the weight of the brain. The more dilute the solution, the greater will be the increase.

For this fact no interpretation has been offered as yet. In 1 % formol the increase of the weight may be 23 %; in 5 % formol 9—10 %; and in 10 % formol 2—3 %. Strong alcohol diminishes the weight through dehydration. After all these circumstances have been duly regarded, there still remains full play for inevitable errors. This, however does not derogate from the important ultimate conclusion, viz. that the weight of the brain of wild canides is considerably below that of domestic dogs. This difference had already been demonstrated before KLATT, e.g. by DARWIN as early as 1878. KLATT has reconfirmed it, and mentions a difference of 20 %. His comparative study of the brain-surfaces has shown that the *lobi frontales* of the house-dog are larger than those of the wolf and of

the jackal. KLATT fixes upon the fissura cruciata as the hind-border. This is not correct from a comparative anatomical point of view, because the sulcus centralis Rolandi, which constitutes in man the hind-border of the frontal lobe, cannot be put on a par with the fissura cruciata of canides. Nonetheless this border-line served the purpose in a practical way, firstly because it exists in all dogs; secondly and chiefly because it contains the very important anterior association centrum. KLATT states that the weight of the frontal-brain of the dog averages about 16 % of the total brain-weight, of the wolf 14.5 %, and of the jackal 15 %. Also the lobi parietales are in the dog heavier than in the undomesticated cognates. On the other hand the lobi olfactorii with the lobi pyriformes and the lobi occipitales are more strongly developed in wild canides than in house-dogs.

The entire postero-inferior border of the hemisphere is more arched in the wolf and the jackal than in the dog; the distance from the splenium corporis callosi to the posterior hemisphere-pole is greater in the first-named animals than in the dog. This warrants the conclusion that in wild specimens the olfactory sense-organ (lobus olfactorius and lobus pyriformis), and the visual sense-organ (area optica in the lobus occipitalis) are more strongly developed than in house-dogs, but that on the contrary important associative centra are most vigorous in the house-dog. This need not surprise us, if we reflect that the mental life of the dog is considerably modified through domestication. Faithfulness, attachment and all that is connected with these qualities, are characteristics of our house-dog, but *not* of his undomesticated cognates.

KLATT has also pointed out distinct differences in the brain-grooves. We shall not enter into the many details he published. Suffice it to say, that the brain surface of wild forms is simpler, displays fewer grooves or less developed corresponding grooves. It is worth noticing that in wild canides the two hemispheres are, almost without exception perfectly similar. This similarity is never met with in the domestic dog. There are intermediate forms. The dogs of negroes and papuans are neglected and maltreated; they remain shy and false; the brains of these dogs have smaller weight and the upper surface of their brains is simpler than e.g. that of Eskimo-dogs, which from their puppyhood upwards live with the family. Thus far KLATT.

Other differences are to be observed when examining under the microscope that portion of the medulla oblongata in which the nucleus hypoglossi and the oliva inferior are situated. For purposes of comparison we selected the oblongatae of domestic animals and

closely related wild animals. In serial sections of from 15—18  $\mu$  the extension has been established of the nucleus XII and of the oliva inferior; for fixed point we took the section in which the canalis centralis of the spinal cord breaks into the fourth ventricle (calamus scriptorius), so that the extension of the nucleus hypoglossi and of the oliva inferior could be told off from the calamus in both directions, toward the spine and toward the cerebrum.

First of all we have to answer the question; is it right to select the calamus for a "point fixe"? Thereby the research stands or falls. I feel confident in answering the question in the affirmative. The nervus hypoglossus is from its origin built up of cervical nerves, of which the sensible roots have got lost. In birds the nucleus hypoglossi still forms one whole with the motor gray-substance of the medulla cervicalis. Such is also the case in the primitive aquatic mammals. Now, when by dint of investigation it has been proved that the nucleus XII of wild animals extends more towards the spine than that of domestic animals, this *may* be induced by a

displacement of the calamus toward the cerebrum. However, if the position of the calamus is unaltered, it *must* be induced by the fact, that this nucleus has not been so far shifted from its original place in wild animals as in domestic animals. That this is indeed the case may be readily proved. In wild animals the first cells of the nucleus XII appear in an area, where remains of the cornu anterius are still clearly noticeable; in domestic animals they appear in an area where these

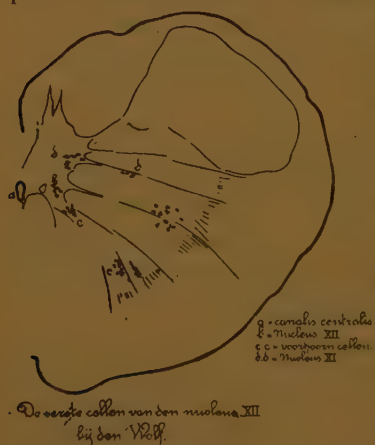


Fig. 1.

remains have long since disappeared (Fig. 1).

We examined: horse-zebra; cow-anoa; sheep-mouflon; dog-wolf-jackal-fox; cat-puma (*felis concolor*); tame rabbit-wild rabbit.

The first two series are of 18, the others of 15  $\mu$ ; cellstaining with toluidin blue or cresil violet.

	spinal ← Nucleus XII → cerebral of the calamus		• Ratio
horse	132	267	1 : 2 +
zebra	174	178	1 : 1 +



This table goes to show that in the horse the cerebral part of the nucleus hypoglossi is as large again as the spinal portion. In the zebra the two parts are equal.

	spinal ← Nucleus XII → cerebral of the calamus		Ratio
cow	119	128	1 : 1 +
anoa	108	68	1 : $\frac{2}{3}$ —

In the cow the cerebral and the spinal parts of the nucleus hypoglossi are of equal size; in the anoa depressicornis, the very primitive wild cow of Celebes, the spinal part exceeds the cerebral by nearly one third.

	spinal ← Nucleus XII → cerebral of the calamus		Ratio
sheep	78	116	1 : $1\frac{1}{2}$ —
mouflon	64	66	1 : 1 +

It is obvious that in the sheep a larger part of the nucleus hypoglossi is situated cerebrad than in the moufflon, the wild sheep of Sardinia.

	spinal ← Nucleus XII → cerebral of the calamus		Ratio
tame rabbit	52	26	1 : $1\frac{1}{2}$
wild rabbit	44	12	1 : $\frac{1}{4}$ +

In the tame and the wild rabbit we find very large differences.

	spinal ← Nucleus XII → cerebral of the calamus		Ratio
cat	40	88	1 : 2 +
puma	84	110	1 : $1\frac{1}{3}$ +

Likewise in the cat and the puma.

	spinal ← Nucleus XII → cerebral of the calamus		Ratio
dog	68	130	1 : 2 —
fox	42	50	1 : 1 +
jackal	48	79	1 : $1\frac{2}{3}$
wolf	96	71	1 : $\frac{3}{4}$
Abyssinian dog	70	96	1 : $1\frac{1}{3}$

From this table it appears that among the canides the wolf reveals very primitive relations, the major portion of the nucleus hypoglossi lying spinal to the calamus; then follows among the wild forms the fox, while the jackal is very much like the house-dog. It is also remarkable that a halfwild Abyssinian dog appeared to possess a rather primitive nucleus hypoglossi.

According to KAPPERS' law of neurobiotaxis the nucleus hypoglossi has broken away from the motor cervical gray matter in order to extend cerebrad in the direction of the gustatory nucleus, situated in the oblongata. We may, therefore, be allowed to assume that the further the nucleus hypoglossi has shifted cerebrad, the more delicate will be gustatory sense-organ, the more the primitive relation to the spinal cord has been preserved, the coarser the sense-organ must be. The gustatory sense-organ, therefore, appears to be less developed in wild forms than in domestic animals.

Also the oliva inferior in wild animals displays remarkable differences as compared with that of domestic animals. Irrespective of a few exceptions we see that in tame animals this complex of nuclei extends further cerebrad than in wild animals.

This is illustrated in the following table: (See page 829).

The moufflon and the jackal form the exceptions. In the moufflon the ratio is just the other way, the inferior olive extends considerably further towards the cerebrum than in the sheep. This may perhaps be accounted for, if we bear in mind that the moufflon is a mountain-animal, so that a greater strain is put upon his cerebellar systems, so also upon his tractus olivo-cerebellares, than upon those of our tranquilly-living sheep. As to the jackal, also his nucleus hypoglossi bears a greater resemblance to the dog-type than that of other wild canides. Considering the fact that his associative brain-centra are more strongly developed than those of the wolf, we are justified in

	spinal ← Oliva inferior → cerebral of the calamus		Ratio
horse	58	375	1 : 6 $\frac{1}{2}$ —
zebra	116	268	1 : 2 $\frac{1}{3}$ —
cow	78	190	1 : 2 $\frac{2}{5}$ +
anoa	108	146	1 : 1 $\frac{1}{3}$ +
sheep	113	194	1 : 1 $\frac{2}{3}$ +
moufflon	54	116	1 : 2 +
tame rabbit	44	42	1 : 1
wild rabbit	54	2	almost entirely spinal
cat	40	108	1 : 2 $\frac{2}{3}$ +
puma	106	172	1 : 1 $\frac{2}{3}$ —
dog	82	168	1 : 2 +
fox	70	56	1 : $\frac{3}{4}$ +
jackal	61	136	1 : 2 $\frac{1}{4}$ —
wolf	132	107	1 : $\frac{3}{4}$ +
Abyssinian dog	86	122	1 : 1 $\frac{1}{2}$ —

concluding that the jackal is more akin to the dog than the wolf is.

Also in respect of subordinate parts of the oliva complex, wild forms display primitive differences. Descriptive anatomy distinguishes principal-, and accessory olivary bodies. This differentiation is absolutely erroneous, for those so-called accessory olivary bodies are not additional, still less accessory; for phylogenetically they are oldest. The medial accessory oliva occurs already in fishes, the dorsal accessory oliva appears already in reptiles, while the so-called principal oliva is characteristic of mammalia. In all mammalia the medial-, and the dorsal-accessory oliva extends further spinally than the ventro-lateral principal oliva. We see then, that the spinal extension of the phylogenetically oldest parts of the oliva-complex, is much more marked in wild forms than in domestic animals. In Ungulates the principal oliva lies exclusively frontal to the calamus, in the horse and the cow, however, it is situated more frontal than in the zebra and the anoa. In the wild rabbit the principal oliva lies spinal to the calamus, in a tame rabbit almost quite cerebrad of it. This is clearly illustrated in the subjoined schemata:

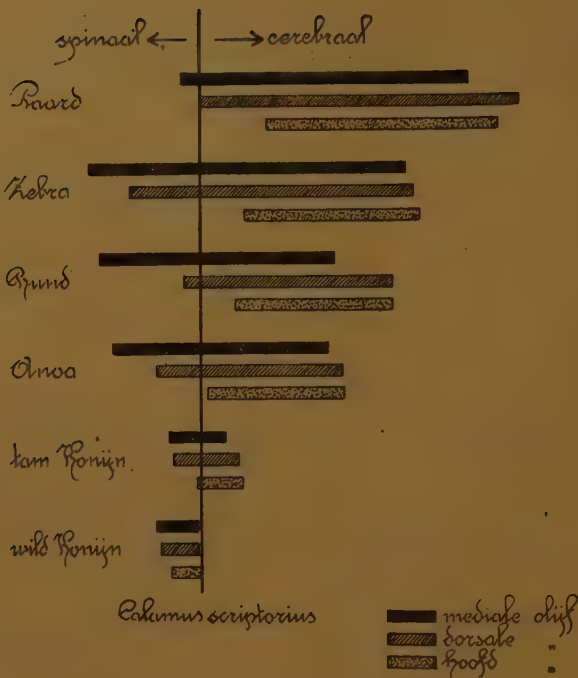


Fig. 2.

When examining the oblongatae of domestic animals in one or more stages of development we shall see that the nucleus hypoglossi and the oliva inferior of these animals ontogenetically pass stages, which persist in wild animals.

I have been in a position to perform the above researches also on material from man and a couple of man-apes. The oliva inferior in primates extends into the pons-area. In these cases not only the oblongatae, but also the pontes have been incised serially. We examined man (West-European), Hottentot, child of 1½ years, foetus of 4½ months, orang-utan, and chimpanzee.

It is evident from the data that the nucleus hypoglossi of the Hottentot compared with that of the West-European, is indeed of a primitive character. The data also show that, in respect of the Nucleus XII and the oliva inferior, the chimpanzee stands nearer to man than the orang-utan, to which fact anthropologists have long since called attention. The differences between the extension towards the cerebrum of the olivæ inferiores in the West-European man and in the chimpanzee are not so large as to be of great physiological importance.

It strikes us that also here the chimpanzee appears to be more human than the orang-utan. It may be worth while to ascertain whether the observed differences in the extension of the oliva



inferior correspond with possible differences on the respective cerebella. In this case we might also establish in this way the

	Nucleus XII			Oliva inferior		
	spinal	cerebr. o. t. calamus	Ratio	spinal	cerebr. o. t. calamus	Ratio
Horse	132	267	1 : 2 +	58	375	1 : 6½ —
id. foetus 5 m.	63	79	1 : 1¼ +	57	110	1 : 1¼/5 +
id. foetus 10 m.	88	118	1 : 1⅓ —	44	220	1 : 5
id. foetus 12 m.	133	176	1 : 1⅓	42	260	1 : 6⅓ +
Cow	119	128	1 : 1 +	78	190	1 : 2½/5 +
id. foetus 4½ m.	110	75	1 : 2/3 +	114	137	1 : 1⅓/5 +
id. neonatus	164	118	1 : 3/4 —	94	196	1 : 2 +
Sheep	78	116	1 : 1½	113	194	1 : 1½/3 +
id. neonatus	88	60	1 : 2/3	107	96	1 : 5/6 +
Dog	68	130	1 : 2 —	82	168	1 : 2 —
id. neonatus	34	48	1 : 1½	40	58	1 : 1½ —

	Nucleus XII			Oliva inferior		
	← spinal	cerebr. o. t. calamus →	Ratio	← spinal	cerebr. o. t. calamus →	Ratio
Man (W. Eur.)	20	190	1 : 9½	92	311	1 : 3⅓ +
Hottentot	45	202	1 : 4½	106	333	1 : 3 +
Chimpanzee	37	108	1 : 3 —	44	178	1 : 4
Orang-utan	61	72	1 : 1⅓ +	85	135	1 : 1½ +
Man	20	190	1 : 9½	92	311	1 : 3⅓ +
Child 1½ year	42	62	1 : 1½ —	56	82	1 : 1½ —
Foetus 4½ m.	44	64	1 : 1½ —	60	96	1 : 1⅓/5

relations of the medial and the dorsal olivæ to the palæo-cerebellum, and those of the principal oliva to the neo-cerebellum.

*From the Anatomical Laboratory of the Veterinary  
University of Utrecht.*

**Biochemistry.** — "*Determination of Carbon-monoxide in blood.*"

By Dr. D. G. COHEN TERVAERT. (Communicated by Prof. C. EYKMAN).

(Communicated at the meeting of October 25, 1924).

GRÉHANT<sup>1)</sup> has probably been the first to estimate carbon-monoxide in blood that has for a smaller or greater part been saturated with this gas. He liberated the gas with a simple mercury-pump and determined the content of CO in his "grisoumètre", a sort of combustion-pipette.

NICLOUX<sup>2)</sup> a pupil of GRÉHANT's determined in the gas liberated with the use of the mercury-pump, the content of CO by leading this gas over Iodine-pentoxide heated at 150°. The Iodine liberated was estimated colorimetrically, being absorbed in chloroform. HALDANE<sup>3)</sup> determined the CO-content of blood by comparing its violet tint with solutions of carmine. PLESCH<sup>4)</sup> and after him GAD-ANDRESEN<sup>5)</sup> liberated the CO together with oxygen from the blood by the use of potassium-ferricyanide as indicated by HALDANE<sup>6)</sup> in the apparatus resp. of BARCROFT and KROGH. The CO was estimated by combustion using a platinum wire which was fitted unto these apparatus.

HARTRIDGE<sup>7)</sup> made an ingenious instrument on the principle of the difference in place of the absorption-bands in the spectra of CO- and oxyhaemoglobin, with the use of which he measured the relative quantities of CO-haemoglobin. When however less than one tenth of the haemoglobin is saturated with CO, all these methods are lacking in accuracy, except probably the method of NICLOUX's, about which no control-experiments are to be found.

In the following way I succeeded in making these determinations with sufficient accuracy.

A wide-mouth flask of 1 Liter capacity is used for extracting the

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<sup>1)</sup> 1894 N. GRÉANT, *Les gaz du sang*, G. MASSON, GAUTHIER—VILLARS et fils (PARIS).

<sup>2)</sup> 1898 *Archives de physiologie normale et pathologique*, 5th series, vol. X, 377.

<sup>3)</sup> 1895 *The journal of physiology*, 18, 463.

<sup>4)</sup> 1914 *Berliner klinische Wochenschrift*, 1957.

<sup>5)</sup> 1916 *Biochemische Zeitschrift*, 74, 357.

<sup>6)</sup> 1897 *The journal of physiology*, 22, 298.

<sup>7)</sup> 1912 *Ibidem*, 44, 1.

CO from the blood with the use of Potassium ferri-cyanide. The flask is closed by a rubber stopper through which pass 3 glass-tubes, all closed with a rubber tube and a screw clamp. Before the blood is introduced the flask is evacuated with the use of a suction-pump. The blood (about 10 c.c.) is then introduced by placing a funnel on one of the tubes and pipetting the blood into it. When the screw-clamp is opened, the blood is sucked into the flask. After the blood 1.5 its volume of water is introduced, mixed and after it 4 c.c. of saturated potassium-ferricyanide. The flask is shaken and placed at 40° (C.) during half an hour, being shaken at intervals. After that time the flask is taken out of the bath and outdoor air is let in by opening one of the clamps and mixed with the contents of the flask. The gas-mixture is now led over Iodine-pentoxide heated at 150° in an oil-bath passing first over concentrated NaOH and then over strong sulfuric-acid before it reaches the  $I_2O_5$ . The Iodine liberated is retained in K. J. and titrated with Thiosulfate. 1 c.c. N/10 Thiosulfate = 5.6 c.c. CO.

In this way I got the following results:

c.c. CO in 10 c.c. Blood.	
Calculated <sup>1)</sup>	Found
0.046	0.058
0.077	0.095
0.115	0.112
0.122	0.122
0.126	0.126
0.180	0.200
0.195	0.215
0.605	0.614
0.647	0.685
0.658	0.602
1.294	1.225
1.294	1.289
1.324	1.316

<sup>1)</sup> Starting from blood of a known CO-content and mixing it with blood of another or no CO-content.

**Palaeo-botany.** — “*Some remarks concerning the classification and the nomenclature of the Inversicatenales*”. By O. POSTHUMUS.  
(Communicated by Prof. J. C. SCHOUTE).

(Communicated at the meeting of November 29, 1924).

When reading the literature in drawing up an index <sup>1)</sup> of the group of fern-like palaeozoic plants, referred to by different authors as Botryopteridaceae, Coenopterideae and other names, my attention was drawn, in the sometimes rather complicated nomenclature, to a few points which led me to make the following remarks.

1. In the title I have indicated this group as the Inversicatenales. This name was given in 1904 by C. EG. BERTRAND and F. CORNAILLE <sup>2)</sup> to a group of palaeozoic plants which had been named Botryopteridaceae by RENAULT, after the genus Botryopteris, which was the genus best known to him. RENAULT <sup>3)</sup> grouped in this family also some stems, which he considered to belong to the genus Zygopteris Corda. In a later publication he also brought into this group Graminatopteris, from which the stem and the surrounding leaf-bases were known, and Dineuron and Diplolabis, then only known by their petioles <sup>4)</sup>.

This classification has been adopted by SCOTT <sup>5)</sup>, TANSLEY <sup>6)</sup> and others, but they subdivided this order or family into the sub-groups Zygopterideae and Botryopterideae. None of the authors doubted the fern-nature of these fossil plants.

In 1904 C. EG. BERTRAND and F. CORNAILLE suggested the name Inversicatenales for this group of plants. When investigating the leaf-trace in the living ferns, they came to the conclusion <sup>7)</sup>, that the units, of which the leaf-trace is built up, are in the petiole

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<sup>1)</sup> To be published as a part of „Fossilium Catalogus” (W. JUNK, Berlin).

<sup>2)</sup> Compt. Rend. Acad. des Sciences., Paris, CXXXIX, p. 347.

<sup>3)</sup> Cours de botanique fossile III, 1883, p. 100.

<sup>4)</sup> Bassin houiller et permien d'Autun et d'Epinac, IV, 1896.

<sup>5)</sup> Studies in fossil botany, ed. I, 1900, ed. II, 1909.

<sup>6)</sup> New Phytologist, VI, 1907, p. 53.

<sup>7)</sup> Mém. et Trav. de l'Univ. de Lille, X, mém. 23, 1902.



arranged in an arc. This arc has, in the living ferns, its concavity directed towards the stem. In the group of plants, mentioned above, the concavity is either directed away from the stem, or the different forms may be derived from such a plant. The name *Inversicatenales* has not been adopted generally; this is perhaps also due to the complicated way, in which the authors expressed their conclusions. The *Inversicatenales* are identical with the *Botryopteridaceae* of RENAULT.

In 1906 <sup>1)</sup> Arber discussed the phylogeny of the ferns; for the palaeozoic representatives of this group, from which the recent ferns must have sprung, he proposed the name *Primofilices*. Though this name may be very useful, this group is not clearly defined by the author.

In 1910 SEWARD <sup>2)</sup> did not adopt this name, and taking the generalised character of many of these forms into account, he suggested the name *Coenopterideae*.

None of these authors has grouped the *Psaronieae* and the permian *Osmundaceae* with the forms mentioned. If it be wished to place the fern-like palaeozoic plants, excepting the *Psaronieae* and the *Osmundaceae*, into one group, one has to choose between the names *Inversicatenales*, *Primofilices* and *Coenopterideae*, for the name *Botryopteridaceae* should be restricted to *Botryopteris* and allied forms. To all these names the objection can be made, that they have been chosen from one certain point of view. Therefore none of them is better than the other. On grounds of priority, however, *Inversicatenales* may be preferred, but one should always bear in mind that it is a collective group only, in which a number of families is grouped together, the affinities of which are rather distant, and may, for instance, be compared with those of the recent *Osmundaceae* and the *Gleicheniaceae*.

2. This group was early subdivided into two groups, the *Botryopterideae* and the *Zygopterideae*, after the only two then known genera. To the first group belong *Botryopteris*, *Grammatopteris*, *Tubicaulis* and *Anachoropteris*. P. BERTRAND <sup>3)</sup> separated the latter genus into a distinct family, the *Anachoropteridaceae*, which he considered to be distinct from the family *Botryopteridaceae*, to which belong the genera *Botryopteris*, *Grammatopteris* and *Tubicaulis*. He looked upon the *Zygopterideae* as a distinct family. Except the genus

<sup>1)</sup> *Ann. of Botany*, XX, p. 218.

<sup>2)</sup> *Fossil Plants*, II, p. 432, 1910.

<sup>3)</sup> *Étude sur la fronde des Zygopteridées*, Thèse, Lille, 1909, p. 199.

*Zygopteris*, restricted by him to *Z. primaria*, he brought into this family a number of genera. These, however, may be conveniently divided into two groups, which have the pinnae on the rachis in 2 or 4 rows respectively. With this morphological character certain anatomical features are correlated.

In the forms with 4 rows of pinnae the peripheral loop, the downwards prolongation of the pinna-bar, has always an interruption above the insertion of the pinna-traces or of the pinna-bar. In the other forms this is never the case. This distinction, which is also found in the grouping of these forms by KIDSTON and GWYNNE-VAUGHAN<sup>1)</sup> and in P. BERTRAND'S schemes<sup>2)</sup>, caused SAHNI<sup>3)</sup> to distinguish two sub-groups, the *Dineuroideae* and the *Clepsydroideae* respectively. These differences seemed to me<sup>4)</sup> to be great enough to raise these groups of plants to the rank of families, the *Dineuroideaceae* and the *Clepsydrosidaceae*.

The genus *Stauropteris* however, is distinct from both groups, as to its mode of ramification<sup>5)</sup> and by its anatomical structure. It is perhaps best to consider these plants as representatives of a distinct family, the *Stauropteridaceae*.

All together one may distinguish 5 different families, which are rather independent of each other. *Silesiopteris* n. gen. (*Gyropteris* Goeppert non Corda) and *Mesoneuron* Unger, of which relatively little is known, can not be included in this classification.

3. If we accept the rules of priority, there appears to be reason, based upon recognised identifications, for new combinations of names, as follows:

a. In 1885<sup>6)</sup> FELIX mentioned the occurrence of a petiole in the Carboniferous of Westphalia, which he described and figured in 1886<sup>7)</sup> as *Rhachiopteris tridentata*. In 1889 WILLIAMSON<sup>8)</sup> described as *Rachiopteris hirsuta* sections of a rhizome and of roots, which SCOTT<sup>9)</sup> proved to belong to the genus *Botryopteris* Renault. *Rhachiopteris tridentata* appeared to be the petiole,<sup>10)</sup> belonging to the rhizome. But as the specific name *tridentata* had been given in

<sup>1)</sup> Fossil Osmundaceae IV, Trans. Roy. Soc. Edinburgh, XLVII, 1910, p. 471.

<sup>2)</sup> *Progressus rei Bot.* II, 1912, p. 224, tabl. II.

<sup>3)</sup> *Ann. of Bot.* XXII, p. 378.

<sup>4)</sup> *Rec. trav. bot. néerl.* XXI, 1924, p. 182.

<sup>5)</sup> Lignier, *Bull. soc. bot. de France*, LIX, 1912, mém. 24, p. 8.

<sup>6)</sup> *Ber. naturf. Ges. Leipzig*, p. 10.

<sup>7)</sup> *Abh. zur geol. Spezialkarte Preussens*, VIII, 3, p. 12, f. 1, 2.

<sup>8)</sup> *Phil. Trans. Roy. Soc. B*, CXXXX, p. 101, f. 9—12.

<sup>9)</sup> *Ann. Report Brit. Assoc. meeting Bristol*, p. 1050.

<sup>10)</sup> Seward, *Fossil Plants II*, 1910, p. 438.

1885 (1886) and *hirsuta* in 1889, this species should be mentioned henceforth as *Botryopteris tridentata*.

b. In 1856 UNGER<sup>1)</sup> described a hollow cortical tube without vascular bundle as *Aphyllum paradoxum*. In 1896 Count SOLMS-LAUBACH<sup>2)</sup> proved, after having studied the original specimen, that the vascular bundle was present, although in another part of it. Its structure was much alike that of *Rachiopteris duplex* of WILLIAMSON<sup>3)</sup> (*Zygopteris duplex* of Tansley<sup>4)</sup>). Therefore P. BERTRAND<sup>5)</sup> made a new genus, *Metaclepsydropsis*, for both forms. This seemed to be necessary because *Rachiopteris* was a collective genus for petiolar remains, and *Zygopteris* was restricted by him to one species only, *Z. primaria*. He<sup>6)</sup> did not accept the generic name *Aphyllum*, because, based upon a hollow cortical tube, it lacked any definition. P. BERTRAND apparently had overlooked that, in 1872, WILLIAMSON<sup>7)</sup> had defined the genus *Arpexylon*, in which he included two species: *A. duplex*<sup>8)</sup> and *A. simplex*<sup>9)</sup>. The former he afterwards named *Rachiopteris duplex*, the latter he proved in 1874<sup>10)</sup> to be a secondary rachis of the former species. These forms have also been mentioned, not only as *Rachiopteris*, *Zygopteris* and *Metaclepsydropsis*, but also as *Aphyllum* and *Arpexylon*. Now one may, as is the opinion of P. BERTRAND, neglect the name *Aphyllum*, because it conveys nothing, but this does not apply to the name *Arpexylon*. In this genus, which corresponds with *Metaclepsydropsis* BERTRAND, two species, *Arpexylon duplex* and *Arpexylon paradoxum* may be distinguished.

c. In 1845 CORDA<sup>11)</sup> gave the name *Gyropteris crassa* to some fossil rests, which were, according to P. BERTRAND<sup>12)</sup>, fragments of petioles from *Psaronieae*. In 1852 GOEPPERT<sup>13)</sup> described and figured a petiole from the Lower Carboniferous from FALKENBERG (Silesia), which he considered also to belong to the genus *Gyropteris* Corda.

1) Denkschr. kais. Akad. der Wiss. Wien Math. naturw. Kl. XI, p. 175, t. 11, f. 1—4

2) Abh. kön. Preusz. Geol. Landesanstalt, N. F. XXIII, p. 30, t. 2, f. 1.

3) Phil. Trans. Roy. Soc. London CLXIV, 1874, p. 688, f. 29—40.

4) New Phytologist, VI, 1907, p. 61, f. 12, 13.

5) Comp. Rend. Acad. des Sc., Paris, CXLV, p. 775.

6) Mém. Soc. d'hist. nat. d'Autun, XXV, 1911, p. 19.

7) Proc. Roy. Soc. London, XX (136), p. 438.

8) l.c., p. 438, f. 1.

9) l.c., p. 438, f. 2.

10) Phil. Trans. Roy. Soc. London, CXLIV, p. 690.

11) Flora der Vorwelt, p. 86, t. 54, f. 1—6.

12) Étude sur la fronde des Zygopt., p. 181. 275.

13) Nov. Act. Acad. Caes. Leop. Car. XXII Suppl., p. 138, t. 11, f. 4—6.

This form, *G. sinuosa*, however, is quite different from *G. crassa*, and certainly does not belong to the *Psaronieae*. It shows some points of agreement with some of the *Inversicatenales* into which group it has been included by P. BERTRAND. As the name *Gyropteris* has been used for the other forms, a new generic name has to be given to *Gyropteris sinuosa* Goepfert, of which only one specimen is known. This genus may be named *Silesiopteris*, with one species only, *Silesiopteris sinuosa*.

*Gröningen.*

*Botanical Laboratory.*

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**Physics.** — "*The structure of solid nitrous oxide and carbon dioxide.*" By J. DE SMEDT and W. H. KEESOM. Communication N<sup>o</sup>. 13 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of March 29, 1924)\*).

### 1. *The structure of solid nitrous oxide*<sup>1)</sup>.

§ 1. In connection with our investigations<sup>2)</sup> on the diffraction of X-rays in liquefied gases, we have worked out a method to get Röntgenograms of solidified gases<sup>3)</sup> at low temperatures. Our first experiments were made with N<sub>2</sub>O and CO<sub>2</sub>, because these gases are already solid at the temperature of liquid air. Moreover they show this particularity that the molecule N<sub>2</sub>O possesses the same number of electrons as the molecule CO<sub>2</sub>. Hence it may be interesting to be able to compare the structures of these substances.

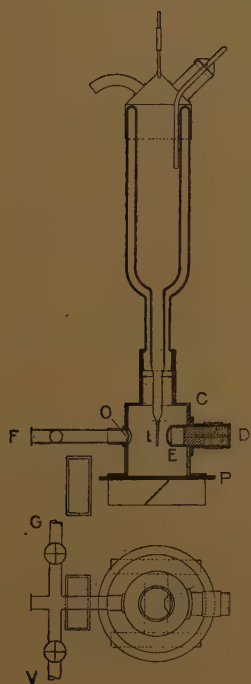


Fig. 1.

§ 2. *The apparatus.* The vacuum glass with fixed to it the camera is only little different from that which has served to the X-ray-diagrams of liquefied gases<sup>4)</sup>. The glass tube *t* (wall thinner than 0.01 mm.) had a diameter of 1 mm. The glass was silvered, excepted the tube *t* and a vertical slit, through which the surface of the liquid could be observed.

The brass tube, which holds the diaphragm of tin (length 4 cm., diameter of the opening 2 mm.) is continued to the inside. It is closed by a small screen with an opening *E*, chosen in such

<sup>1)</sup> In this translation the results of our second communication on this subject have been taken up.

<sup>2)</sup> Comm. N<sup>o</sup>. 10 and N<sup>o</sup>. 12, these Proc. 25, 1922, p. 118, and 26, 1923, p. 112.

<sup>3)</sup> As a subject of research already mentioned in Comm. N<sup>o</sup> 1, these Proceedings 21, 1918, p. 405. Cf. Comm. N<sup>o</sup>. 10. At the same time F. SIMON and CLARA VON SIMSON independently worked out such a method, Zs. f. Phys. 21, 168, 1924.

<sup>4)</sup> Comm. N<sup>o</sup>. 10, these Proceedings 25, 1922, p. 118.

\*) Published in these Proceedings, meeting of June 28, 1924.

a manner that the Röntgen beam, which is limited by the diaphragm, passes without striking the metal, whereas the rays, which are reflected by the tin crystals at the utmost brim of the diaphragm, are intercepted.

To the opening  $O$  of the camera is fixed a glass tube, which is closed at the end by a small window  $F$  of mirror glass.

Of the two side-tubes, one,  $V$ , leads to the vacuum pump, the other,  $G$ , to the container in which the gas to be investigated is stored.

§ 3. *Depositing the crystals.* When a sufficiently high vacuum has been formed in the apparatus, the vacuum glass is filled with liquid air. By closing the tap in  $V$ , the connection with the pump is broken, after which the gaseous  $N_2O$  is admitted through  $G$ . It condenses as a micro-crystalline powder on the narrow tube  $t$ . This condensation could be watched through the window  $F$  by means of a telescope, the crystals being illuminated by the aid of a mirror which was placed under the glass closing-plate  $P$ .

In order to prevent that during the depositing of the nitrous oxide the liquid in the tube  $t$  boils away, during this manipulation a wire of well conducting metal was let in from above.

Depositing was stopped when the crystal layer had obtained a thickness of 0.4 mm.

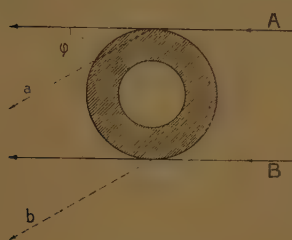
§ 4. *The film*, which was obtained with an exposition of  $2\frac{1}{2}$  hours (30 m. A, 25 KV.) with  $K$ -rays of copper, showed very sharp lines and so proved that the micro-crystals had had the right dimensions. This film was made without a Ni-filter. We owe to Dr. N. H. KOLKMEIJER a second film, with Ni-filter.

The films show no trace of a diffraction ring that could be due to the liquid air in the tube  $t$ .

In the calculation it appeared however that there are parasitic lines on both the films. The rings namely, due to the crystal planes with the smallest indices appeared to be double. This can be explained by the fact, that the crystal powder was irradiated as a relative wide cylinder mantle, which surrounds the tube with liquid air, and not as a thin bar, as is ordinarily the case with the method of DEBIJE and SCHERRER.

In Fig. 2 the hatched ring represents a section through the cylinder mantle, formed by the crystal powder.  $AB$  be the incident beam. If we consider the diffracted rays  $a, b$ , which make a small angle with the direction of incidence, we see that the rays which

are diffracted by the outer surface of the cylinder, have to pass through a much thinner layer of absorbing substance than those rays which pass through the centre. So the beam that is diffracted



in the direction  $\varphi$ , is divided into two smaller ones. Of these the beam, originating from  $b$ , will have the greatest intensity. As  $\varphi$  is larger, the rays from  $a$  must pass through a thicker layer, and so they will finally give no more a visible impression on the film.

Fig. 2.

As was made first for  $\text{CO}_2$  (cf. § 6), afterwards also for  $\text{N}_2\text{O}$  expositions were made with half of the incident Röntgen beam being screened off, in order to identify these parasitic lines indubitably<sup>1)</sup>.

§ 5. *Results.* Table I contains the experimental results, derived from the film ( $K\alpha$ -rays of  $\text{Cu}$ ).

The first column gives the observed intensities. In the second column the radii of the interference rings are inserted, viz. half the distances, measured on the film, of the two interference lines on both sides of the centre. The radius of the film is 27,3 mm. The third column gives  $\sin^2 \frac{\varphi}{2}$ , the correction for the thickness of the irradiated preparation having been applied. This correction is put equal to  $r \cos \frac{\varphi}{2}$ , to be subtracted from the radius of the interference ring,  $r$  being the radius of the outer circumference of the preparation<sup>2)</sup>. The fourth column is relative to the deriving of a common divisor of the values of  $\sin^2 \frac{\varphi}{2}$ . The common divisor 0.0181 gives quotients, which oscillate about whole numbers, excepted however the numbers placed between [ ]. These are relative to parasitic lines as mentioned in § 4. The relative values of the intensities agree with the supposition about their origin made in § 4. The quotients of the fourth column show still a weak tendency to enlarge with encreasing  $\varphi$ . We ascribe it to the circumstance, that somewhat too large values are given to above-said correction terms.

From table I we conclude, that nitrous oxide crystallises cubically

<sup>1)</sup> These expositions were made in the Physical Laboratory at Leiden. Our thanks are due to Mr. V. ESBACH, assistant of this laboratory, for his help in making these expositions.

<sup>2)</sup> Comp. W. GERLACH und O. PAULI, Zs. f. Phys. 7, 116, 1921.

TABLE I.

Intensity <sup>1)</sup>	Radius of the interference ring in $\frac{1}{10}$ mm. <sup>2)</sup>	$10^3 \cdot \sin^2 \frac{\varphi}{2}$ <sup>3)</sup>	$\sin^2 \frac{\varphi}{2} : 0.0181$ <sup>3)</sup>	<i>h. k. l.</i>
f	102	29	[1.60]	
m	115	37	[2.06] <sup>4)</sup>	
f	123 <sup>5)</sup>	44	[2.58]	
vs	136	54	2.97	111
vf	145	61 <sup>5)</sup>	[3.40]	
m <sup>5)</sup>	154	70	3.85	200
vf	161	76	[4.20]	
vs	173	88	4.88	210
s	191	108	5.95	211
m	221	145	8.02	220
f	273	219	12.10	222
m	283	234	12.94	320
m	296	255	14.08	321
vf	316	287	15.83	400
vf	329	310	17.12	322—410
s	349	344	19.05	331
vs	359	361	19.95	420
f	369	380	21.95	421
f	380	399	22.05	332
vf	399	434	24.00	422
vf	420	472	26.04	510—431
m	448	525	29.00	520—432
vf	459	545	30.05	521
s	479	582	32.15	440
s	509	635 <sup>5)</sup>	35.10	531
f	519	654	36.10	600—442
m	540	691	38.15	611—532

<sup>1)</sup> vf = very feeble, f = feeble, m = moderate, s = strong, vs = very strong.

<sup>2)</sup> To the numbers given in the report about the work of the 1st International Commission of the Institut International du Froid, presented to the 4th International Congress of Refrigeration in London, the corrections for the thickness of the preparation had already been applied.

<sup>3)</sup> These numbers are something different from those, given in the report mentioned in note 2, on account of another calculation of the corrections for thickness of the preparation.

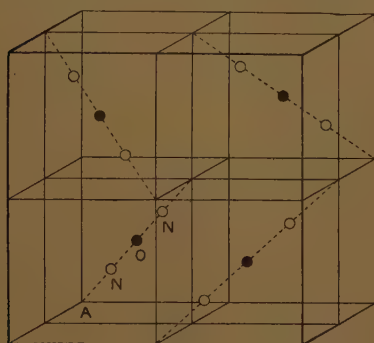
<sup>4)</sup> That this line is a parasitic one was shown by the film made with half of the incident Röntgen beam being screened off.

<sup>5)</sup> That this line has a mean intensity was taken from the film mentioned in footnote 4).



with a side of the unit cube  $5.72 \text{ \AA}^1$ ). In order to calculate the number of the molecules in a unit cube the density of solid nitrous oxide is not available. If we suppose 4 molecules in the unit cube the calculated density is  $1.55^1$ ), whereas, at the melting-point,  $-90.5^\circ$ , the liquid has a density  $1.299$ .

In Fig. 3 we have drawn the structure which for the calculated intensities has given values which agree with the observed ones. On each of the four not intersecting diagonals of the cube, forming the ternary axes, we find a molecule  $\text{N}_2\text{O}$ , viz. an atom  $O$  in the middle of it, on both sides at the same distance flanked by an atom  $N$ .



● O    ○ N

Fig. 3.

As a parameter we chose: the projection  $q$  of the distance between the atoms  $O$  and  $N$ , on the side of the unit cube.

The places of the other atoms follow then from the ternary symmetry of the axis  $AO$ . The parameter is expressed in  $360^{\text{th}}$  parts of the side of the elementary cube. The best agreement of calculated intensities with the observed ones (see table II) has been obtained with  $q = 42$ . In these calculations we

have taken into consideration: 1°. the structure factor, 2°. the factor on account of the number of the planes that contribute to the diffraction, 3°. the LORENTZ-factor, 4°. the factor  $\frac{1}{\cos \frac{\varphi}{2}}$  proposed by BIJVOET<sup>2)</sup>.

The coordinates of the 4 atoms  $O$  are thus:  $\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a$ ;  $\frac{3}{4}a, \frac{3}{4}a, \frac{3}{4}a$ ;  $\frac{1}{4}a, \frac{3}{4}a, \frac{3}{4}a$ ;  $\frac{3}{4}a, \frac{1}{4}a, \frac{1}{4}a$ .

$a = 5.72 \text{ \AA}$ . The distance between two neighbouring atoms  $N$  and  $O$  is  $1.15 \text{ \AA}$ .

## II. The structure of solid carbon dioxide.

§ 6. The expositions for solid carbon dioxide have been made in the same way as those for nitrous oxide (cf. §§ 2—4).

Also an exposition has been made at which half of the incident Röntgen beam was screened off by means of a small screen

<sup>1)</sup> Owing to a repeated calculation these numbers are somewhat different from those which are given in the report mentioned, p. 842, note 2.

<sup>2)</sup> J. M. BIJVOET, Thesis, Amsterdam 1923.

that was placed at a short distance before the preparation, in such a manner that only the right half or the left half of the preparation was irradiated. So a complete interference figure without the

TABLE II.

<i>h. k. l.</i>	Intensity	
	observed	calculated
100	—	0
110	—	0
111	vs	8425
200	m	2282
210	vs	3740
211	s	3230
220	m	1760
300 } 221 }	—	45
310	—	0
311	—	465
222	f	783
320	m	2020
321	m	3325
400	vf	250
322 } 401 }	vf	89
330 } 411 }	—	35
331	s	2630

parasitic lines mentioned in § 4 has been obtained on one side of the film. On the other side only the parasitic lines appeared. So we get in the first place an affirmation of the supposition mentioned there, relative to the origin of the parasitic lines. The parasitic lines could further be identified now indubitably for carbon dioxide.

Table III contains these experimental results. The columns have the same meaning as in table I. The parasitic lines have been omitted.

In the fifth column two planes (311 and 420) have been inserted.

They appeared on another film than the one for which these calculations were made.

From the fact that the quotients in the 4<sup>th</sup>. column oscillate about

TABLE III.

Intensity	Radius of the interference ring in $\frac{1}{10}$ mm.	$10^3 \cdot \sin^2 \frac{\varphi}{2}$	$\sin^2 \frac{\varphi}{2} : 0.0187$	<i>h. k. l.</i>
vs	140	56	3.0	111
f—m	160	74	3.96	200
s	177	91	4.89	201
s	196	112 <sup>5</sup>	6.02	211
f—m	228	153	8.16	220
vf	240	168	8.99	221—300
vf				311 <sup>1)</sup>
vf	281	229	12.25	222
m	291	245 <sup>5</sup>	13.13	320
m	302	262	14.02	321
vf	349	342	18.30	330—411
m—f	358	358	19.15	331
vf				420 <sup>1)</sup>
vf—f	376	391	21.00	421
vf	387	411 <sup>5</sup>	22.01	332
m	458	541	28.98	520—432
vf	469	563	30.09	521
m	487	595	31.85	440
vf	519	651	34.83	531

whole numbers, we conclude that carbon dioxide (just as nitrous oxide) crystallises in the cubic system. The side of the unit cube is 5,63 Å. If we admit the number of the molecules in an elementary cube to be 4, we obtain for the density 1,63, in agreement with the value, which DEWAR<sup>2)</sup> obtained at the temperature of liquid air.

<sup>1)</sup> From another film.

<sup>2)</sup>  $\delta_{-188^\circ} = 1.63$ , Chem. News 85, 277, 1902;  $\delta_{-189^\circ} = 1.627$ , Chem. News 91, 216, 1905.

Hence the structure of carbon dioxide is given by Fig. 3, just as that of nitrous oxide, if *O* has been replaced by *C* and *N* by *O*.

The parameter *q* was chosen in the same way as for nitrous

TABLE IV.

<i>h. k. l.</i>	Intensity	
	observed	calculated
111	vs	6420
200	f—m	1735
201	s	3070
211	s	3100
220	f—m	940
221—300	vf	148
310	—	—
311	vf	102
222	vf	370
320	m	2700
321	m	3400
400	—	430
322—410	—	365
330—411	vf	218
331	m	1520
420	vf	176

oxide. As the line 110 is absent it follows that the atom *C* lies in the middle of the diagonal. The best agreement between calculated and observed intensities was obtained for  $q = 39$  (see table IV).

So the coordinates of the C-atoms are  $\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a; \frac{3}{4}a, \frac{3}{4}a, \frac{3}{4}a; \frac{1}{4}a, \frac{3}{4}a, \frac{3}{4}a; \frac{3}{4}a, \frac{1}{4}a, \frac{3}{4}a$ , *a* being 5.63 Å. The *O*-atoms are at the same distance on both sides of a *C*-atom. That distance *CO* is 1.05 Å.

It is an agreeable duty to us to thank Miss Irm. DESMET, who has made most of the intensity calculations.



**Physios.** — “*The Crystal Structure of Mercuric Sulphide*” II. By Dr. N. H. KOLKMEIJER, Dr. J. M. BIJVOET and Dr. A. KARSSSEN. Communication N°. 15 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of October 25, 1924.)

§ 1. By the DEBYE-SCHERRER method black „*amorphous*”  $HgS$  was found to have  $ZnS$ -structure, with lattice parameter,  $5.85 \text{ \AA}$ .<sup>1)</sup>

§ 2. By the BRAGG method the structure of the trigonal cinnabar was determined by MAUGUIN<sup>2)</sup>: The dimensions of the cell are  $a = b = 4.15 \text{ \AA}$ ,  $c = 9.51 \text{ \AA}$ ; with only slight deviations the particles are arranged on a rhomboedric lattice. DEBYE-SCHERRER photographs of cinnabar made by us confirm completely the structure given by MAUGUIN.

§ 3. There appeared to be a striking agreement between the DEBYE films of the black and the red modifications (see the first photogram on the plate and columns 3 and 8 of the table). The lines of black  $HgS$  are found on the film of the red agreeing in place and for the greater part in intensity ratio, the total number of lines for the latter being larger. One would rather think the red to contain the black. This, however, is excluded by the fact that in the BRAGG method the measurements were made on a single homogeneous crystal. (In the powder method a transformation might occur by pulverising the sample<sup>3)</sup>). *The agreement is caused by the complete equality of the dimensions in the octahedral- and basis plane of the regular resp. trigonal modification.* In these alternating  $Hg$ - and  $S$ -planes the particles are arranged in centered regular hexagons with sides  $\frac{1}{2} \sqrt{2} a_{black} = 4.14 \text{ \AA} = a_{red}$ .

<sup>1)</sup> N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSSEN. These Proceedings 27, p. 390 1924 Rec. trav. chim. 43, 677, 1924.

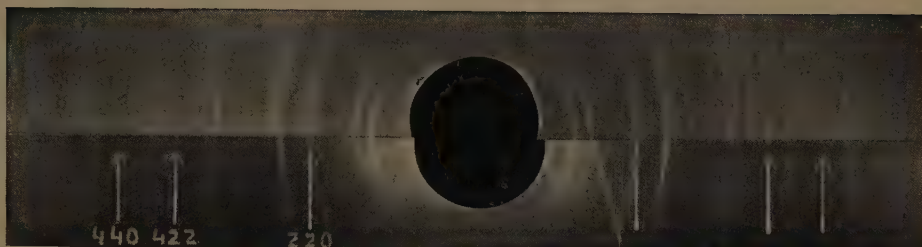
<sup>2)</sup> CH. MAUGUIN, Compt. rend. 176, 1483, 1923.

<sup>3)</sup> L. VEGARD. Z. Physik 5, 393, 1921.

Black HgS				By reducing in the direc- tion of c splitted up into	$10^3 \sin^2 \frac{\varphi}{2}$ (calculated)	Red HgS	
Nr.	Indices	$10^3 \sin^2 \frac{\varphi}{2}$ (observed)	Intensi- ties			Intensi- ties	$10^3 \sin^2 \frac{\varphi}{2}$ (observed)
1	2	3	4	5	6	7	8
1	111	52	vs	$\overline{1011}$	53	vs	54
				$\overline{0003}$	60	vf	59
2	200	69	f	$\overline{1012}$	72	vs	72
3	220	139	vs <sup>—</sup>	$\overline{1120}$	139	s	141
				$\overline{1014}$	152	ms	155
4	311	191	vs	$\overline{2021}$	192	vs	196
				$\overline{1123}$	199		
				$\overline{1015}$	212	s	212
5	222	208	vf	$\overline{2022}$	211	„	„
				$\overline{0006}$	238	f	241
6	400	278	vf	$\overline{2024}$	291	fm	289
7	331	330	m	$\overline{2311}$	324	s	327
				$\overline{2025}$	351	ms	350
				$\overline{1017}$	370		
8	420	347	m	$\overline{1232}$	350	„	„
				$\overline{1126}$	377	ms <sup>—</sup>	377
9	422	416	m	$\overline{3030}$	416	f	420
				$\overline{2134}$	430		
				$\overline{1018}$	470	m+	466
10	333 511	468	m	$\overline{3033}$	476	m	479
				$\overline{1235}$	490		
				$\overline{2027}$	509	vf	504
11	440	555	f <sup>—</sup>	$\overline{0009}$	536		
				$\overline{2240}$	555	fm	555
				$\overline{2028}$	609		

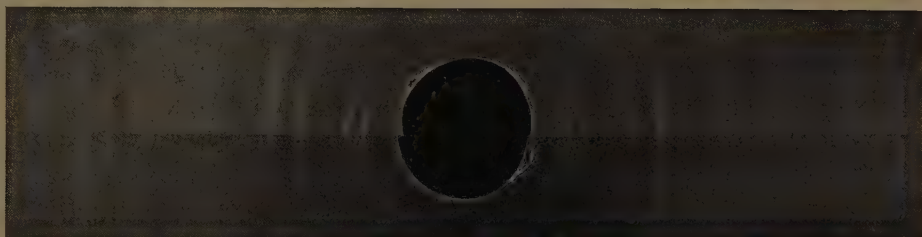
N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSEN: "The Crystal Structure of Mercuric Sulphide". II.

Cinnabar



„Amorphous” HgS

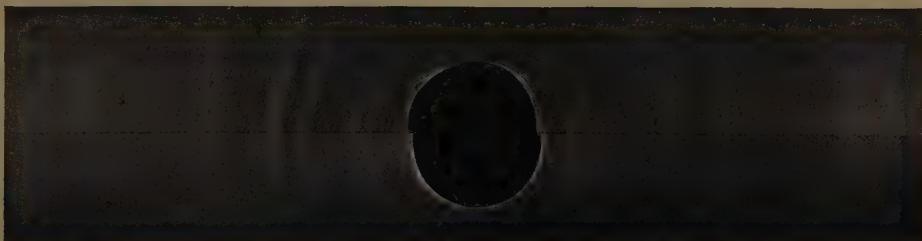
Cinnabar



50% cinnabar

50% „amorphous”

Cinnabar



$\beta'$  HgS





For the face-centered cubic modification the expression for  $\sin^2 \frac{\vartheta}{2}$  reads after transformation to trigonal axes:  $\frac{8}{3} A (h_1^2 + h_2^2 + h_1 h_2) + \frac{1}{3} A h_4^2$ : for the black *HgS*  $A=17.35$ ,<sup>1)</sup> hence

$$\sin^2 \frac{\vartheta}{2_{black}} = 46.27 (h_1^2 + h_2^2 + h_1 h_2) + 5.78 h_4^2. \quad (1)$$

Now we assume  $A_{red}$  to be *exactly* equal to the corresponding value of the black modification (for justification see below), the first constant in the expression  $\sin^2 \frac{\vartheta}{2_{red}}$  thus obtaining the same value 46.27.

Then the value 6.62 for the second constant gives the diffraction angles of column 6,  $c$ -value = 9.46 Å, and density 8.24; these values closely correspond with the observed diffraction angles of column 8, MAUGUIN's  $c$ -value 9.51 Å and the values of the density given in the literature (about 8.1<sup>2)</sup>). Hence:

$$\sin^2 \frac{\vartheta}{2_{red}} = 46.27 (h_1^2 + h_2^2 + h_1 h_2) + 6.62 h_4^2. \quad (2)$$

According to equations (1) and (2) the shortening of the trigonal axis will give a clear difference in diffraction angle only for the planes  $h_4 > 2$ , as appears from column 3 and 6. Column 5 gives the planes in which those of column 2 are split up by the trigonal transformation.

To decide to which degree the dimensions in basis or octahedral plane are equal, we compared as exactly as possible the diffraction angles of the planes for which the trigonal axis is zone-axis. Measuring separate films of both modifications the exactness is diminished by differences in thickness and excentricity of the rod and in the change of length of the films by their treatment. This was avoided by exposing a mixture of 50 % black and 50 % red; *no widening of the lines was observed for the mentioned zone* (see second photograph of the plate: the planes of this zone are marked on the first photograph. *So the angles of these reflections appear to differ less than some tenth m.m. for both modifications, the dimensions in the basis plane thus agreeing within some tenth percents.*

<sup>1)</sup> N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSEN l.c.

<sup>2)</sup> LANDOLT-BÖRNSTEIN, Physik. Chem. Tabelle. 4e Aufl. p. 182.

§ 4. *Comparison of the Structure of the Trigonal and Cubic Modifications.*

We found the same arrangement and exactly the same dimension in octahedra or basis plane. Thus the difference between the regular and hexagonal modifications consists only in the manner in which these planes are piled up, at least as regards the arrangement of the centres of the particles. A similar behaviour is found, inter alia, in some allotropic forms which crystallize cubically and hexagonally close packed (Co, Ce), and in the cubic zincblende and hexagonal Wurtzite. But in these cases in both modifications the relative position of neighbour planes is the same, the tetrahedral grouping of the particles being preserved. In the case of HgS on the contrary in the trigonal modification, the piling up of the basis planes differs much more and the tetrahedral arrangement is lost (the distance of the basis planes too being changed). So in this case the equality of the dimensions in the octahedral or basis plane is still more remarkable.

§ 5. By X-ray analysis none of the different HgS modifications described by ALLEN and CRENSHAW were found to contain crystals different from those of the ordinary black and red forms. The third diagram of the plate gives the comparison of the films of red and  $\beta'$ -HgS, the latter being mentioned by these investigators as a doubtless new modification.

§ 6. We intend to examine whether the natural black HgS — the regular metacinnabariet — is identical in crystalstructure with black „amorphous” HgS, as soon as this material will be at our disposal.

§ 7. *Summary.* The cubical (black) and trigonal (red) mercury-sulphide have exactly the same dimensions in the octahedral or basis plane. This explains the striking agreement between their DEBYE-SCHERRER photograms.

$\beta'$ -HgS nor any other of the modifications mentioned by ALLEN and CRENSHAW form a new modification.

For the preparation of the several HgS forms we wish to express here our hearty thanks to Mr. J. RINSE, chem. doct. Amsterdam, who is occupied with a thermodynamical study of the system HgS.

Utrecht, }  
Amsterdam, } 27 October 1924.

**Zoology.** — “On the development of the larva of the fourth stage of *Strongylus edentatus* (Looss)”. By Prof. J. E. W. IHLE and Dr. G. J. VAN OORDT. (Communicated by Prof. C. PH. SLUITER.)

(Communicated at the meeting of November 29, 1924).

In connection with our former publication (1924, p. 194) on the development of the 4<sup>th</sup> larval stage of *Strongylus* (*Delafondia*) *vulgaris*, we now have investigated the development of this stage in *Strongylus* (*Strongylus*<sup>1</sup>) *edentatus*.

The larva of this species lives by preference in the subserosa of the peritoneum parietale of the horse and has been studied especially by O. MARTIN (1910). The larva living under the peritoneum undoubtedly belongs to the fourth stage and is also considered to belong to this stage by RAILLIET (1923, p. 383). It passes over into the young animal (5<sup>th</sup> stage) by a moult. This moult takes place during the stay of the larva under the peritoneum parietale, where the young animals are also to be found, consequently.

According to MARTIN (1910, p. 126) the “young” larvae (i.e. the larvae of the 4<sup>th</sup> stage) moult at least twice under the peritoneum parietale. This investigator holds that no changes take place during the first moult; by a second moult the larva passes over into the young animal. We do not understand what MARTIN means by this first moult; we were unable to find any trace of it.

The larva of the third stage is not yet known, nor the one of *Strongylus vulgaris*. Neither do we know, where the ecdysis takes place, by which the 3<sup>rd</sup> stage passes over into the 4<sup>th</sup> stage.

Our material is not very extensive and has been collected by the Commission appointed to inquire into the Sclerostomiasis in Holland and in the Pathological Institute of the School of Veterinary Medicine at Utrecht.

The youngest larvae, found in this material and of which we assume that they belong to *S. edentatus*, were met with in the liver of a young horse, dissected in the Pathological Institute of this

<sup>1</sup>) Recently one of us (IHLE, 1924) attempted to show that it is not desirable to create a separate subgenus (*Alfortia* Railliet, 1923) for *S. edentatus* but that *S. edentatus* and *S. equinus* must be united in the subgenus *Strongylus* Railliet.

School. The dissection protocol mentions: "lying without reaction in the liver-parenchym."

The presence of such larvae in the liver supports the opinion that they are transported by the bloodcirculation. However, there are two possibilities: either after the infection of the horse the larvae have pierced the gut-wall and are carried by the vena portae to the liver, where they have stayed abnormally, or the larvae have passed through the liver normally and have come through the heart and lungs into the aorta and are transported accidentally from this artery to the liver instead of to the peritoneum parietale. Young specimens of *S. edentatus* were also found by MARTIN (1910, p. 136) in the liver; they belonged, however, to the 5<sup>th</sup> stage (the worm

not yet mature). GLAGE (1906), MARTIN (1910) and RAUILLIET (1923) are also of opinion that the larvae reach the peritoneum parietale normally through liver, heart, lungs and arteries.

The (6) larvae from the liver, investigated by us and belonging in all probability to the 4<sup>th</sup> stage, have a length of 3.8—5 mm. and a maximum thickness of 325—360  $\mu$ . A short, funnelshaped mouth-cavity, the wall of which passes over into the lining of the oesophagus leads directly into the oesophagus. In a few specimens the mouth-opening is at the bottom of a shallow, funnelshaped pit, covered by the cuticle of the body. This pit is probably formed during fixation. The slender oesophagus has a length of 460—

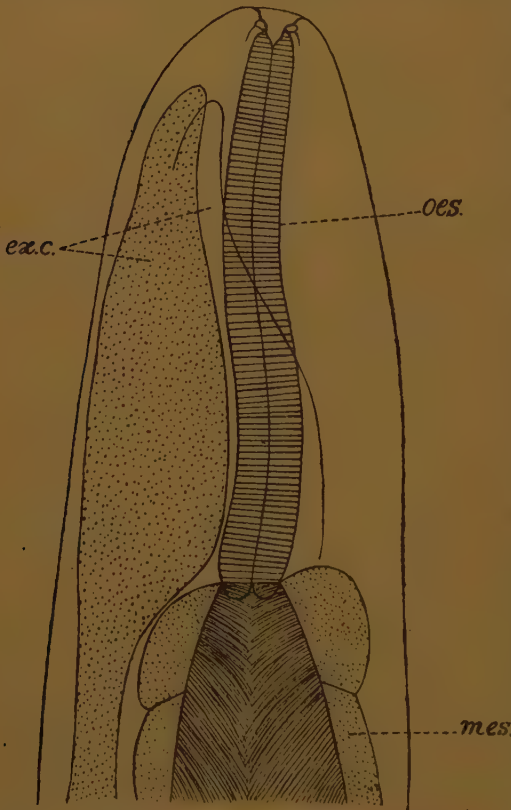


Fig. 1. Anterior extremity of a young larva of *S. edentatus* (long 5 mm.) from the liver. ( $\times 135$ ).

560  $\mu$ , with a maximum thickness of 85  $\mu$ . The anterior part of the mesenteron is much broader than the oesophagus. The cells of the mesenteron possess a striated lining being very high, especially in the beginning of the mesenteron. The rectum is



short; in the largest specimen the anus is situated only  $45\ \mu$  from the posterior extremity (measured along the body-axis). The material is not extensive enough for us to state whether or not this extremity shows sexual differences. These larvae must be considered to belong to *S. edentatus* because they possess two large excretory cells (cervical glands), situated subventrally and being very conspicuous. The anterior extremity of these cells is situated close to the mouth-opening (in the largest specimen at a distance of  $85\ \mu$ ), the posterior extremity far backward (in the largest specimen  $1370\ \mu$  from the posterior extremity). Both anterior extremities of these excretory cells are situated at the same distance from the mouth; the posterior extremity of one of these cells can reach much further backward than that of the other (in one of our specimens this difference was  $300\ \mu$ ).

The older larvae, investigated by us, are found under the peritoneum (especially under the peritoneum parietale). The smallest of these specimens has a length of 4.3 mm. and a maximum thickness of  $325\ \mu$ ; the largest, female larvae have a length of 17 mm. and a maximum thickness of  $950\ \mu$ . The larvae of *S. edentatus* are relatively thicker than the larvae of *S. vulgaris*. MARTIN (1910, p. 123) found larvae without sexual characteristics of 4—7 mm., male larvae of 6—15 and female larvae of 7—18 mm. in length. Here we intend to give a description of the larvae, situated under the peritoneum and belonging to the fourth stage.

The anterior extremity is provided with a plate (figs. 2—4), which can be compared to the mouth-rosette of *S. vulgaris* and which is described by MARTIN (1910, p. 124) under that name. According to the description of that author, the rosette consists of an internal, strongly refractive ring around the mouthopening and of an external zone of the same breadth. We also observed a strongly refractive internal ring, which is much narrower than the external zone, however. This internal ring is the optical section of the wall of the funnelshaped mouth-cavity. According to MARTIN the rosette mostly possesses four lobes, separated from each other by incisions of the external margin. The two largest lobes are divided into two parts, separated by small incisions. Consequently the whole rosette possesses, more or less distinctly, 6 lobes. According to MARTIN the rosette can also have a totally smooth margin. In our preparations, rendered transparent in creosote and in which the anterior part of the body was cut off, the margin of the mouth-plate (rosette) was indistinctly visible. In a few cases we observed a six-lobed plate, in other cases the latter had a smooth margin.

We do not understand MARTIN's communication: "Die Lappen" (of the mouth-plate) "tragen an ihrem äusseren Rande lange Wimpern, die in der Mitte des Randes am längsten sind und nach den Enden

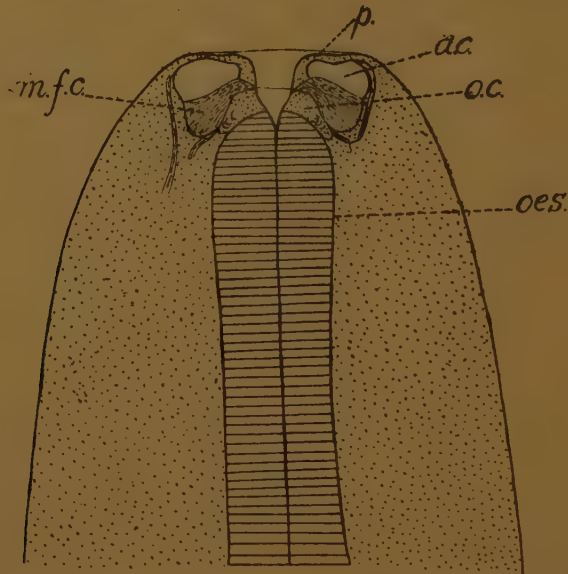


Fig. 2. Anterior extremity of a slightly older larva of *S. edentatus*, long 8 mm. ( $\times 150$ ).

zu kürzer werden". RAILLIET (1923, p. 383) using MARTIN's description, speaks of "quatre lobes, bordés en dehors de très fines lamelles". It is impossible that hairs ("Wimpern") occur at the margin of the mouth-plate. MARTIN's "Wimpern" are possibly muscle-fibres, as the somatic musculature extends forward as far as the mouth-plate.

The mouth leads into a funnelshaped mouth-cavity, which passes over into the lumen of the oesophagus. A separate mouth-vesicle, mentioned by M. SCHLEGEL (1907, p. 54) and by MARTIN (1910, p. 124) does not occur in the larva of *S. edentatus*, nor in the larva of *S. vulgaris* (IHLE & VAN OORDT, 1924, p. 252). The anterior part of the mouth-funnel is surrounded by the mouth-plate, which moreover shows a circular thickening around this funnel. The following part of the mouth-funnel is surrounded by a peculiar tissue, which we call mouth-funnel-collar (figs. 2—4) and which will be described more in detail lower down. Finally the posterior part of the funnel is surrounded by a tissue, which may entirely be compared to the oesophagus-collar of the larva of *S. vulgaris* (IHLE & VAN OORDT, 1924, p. 253). This collar surrounds the anterior part of the oesophagus; however, it is not so well set off backwards as in *S. vulgaris*.

Just as in young larvae of *S. vulgaris* of the fourth stage (IHLE

& VAN OORDT, 1924, p. 254) the formation of the definitive mouth-capsule-cavity is preceded by the formation of an "anterior cavity" (figs. 3 and 4). This cavity is limited in front by the mouth-plate, in young stages posteriorly by the mouth-funnel-collar, mentioned above. The latter consists of delicate lamellae, piled on each other. In the larva

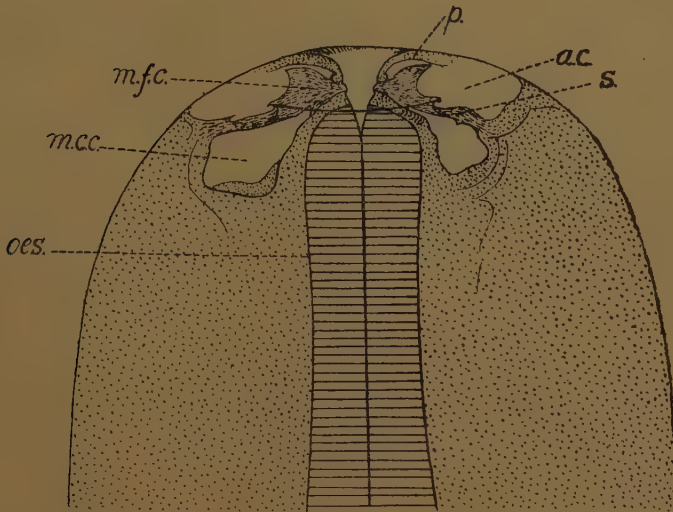


Fig. 3. Anterior extremity of an older larva of *S. edentatus*, long 14.5 mm. ( $\times 93$ ).

of *S. vulgaris* this collar is replaced by a fine, granular substance (IHLE & VAN OORDT, 1924, p. 253), situated in front of the oesophagus collar. In older stages of the larva of *S. edentatus* this anterior cavity extends peripherally, so that the mouth-funnel-collar finally forms a part of the interior lining of this cavity. Behind the anterior cavity the definitive mouth-capsule-cavity arises; just as in the larva of *S. edentatus* both cavities are separated by a septum. The interior margin of this septum passes over into the mouth-funnel-collar, while at the peripheral margin of the septum the definitive mouth collar will develop after the formation of the wall of the definitive mouth-capsule.

An older larva with large anterior cavity and mouth-capsule cavity, of which the wall has been entirely formed, must be mentioned separately (fig. 4). In this specimen the definitive mouth collar is already present but the external leafcrown is not yet visible. The oesophagus-collar has loosened from the oesophagus. We cannot decide whether this took place during fixation or whether it is the beginning of a moult. We may assume, however that this loosening

also takes place, when the worm is moulting, in the same way as we have described in *S. vulgaris* (IHLE & VAN OORDT, 1924, p. 256).

We could not find a septum in a few specimens, which are distinguished by a slenderer shape. In these specimens the anterior cavity and the mouth-capsule-cavity are united. We cannot make

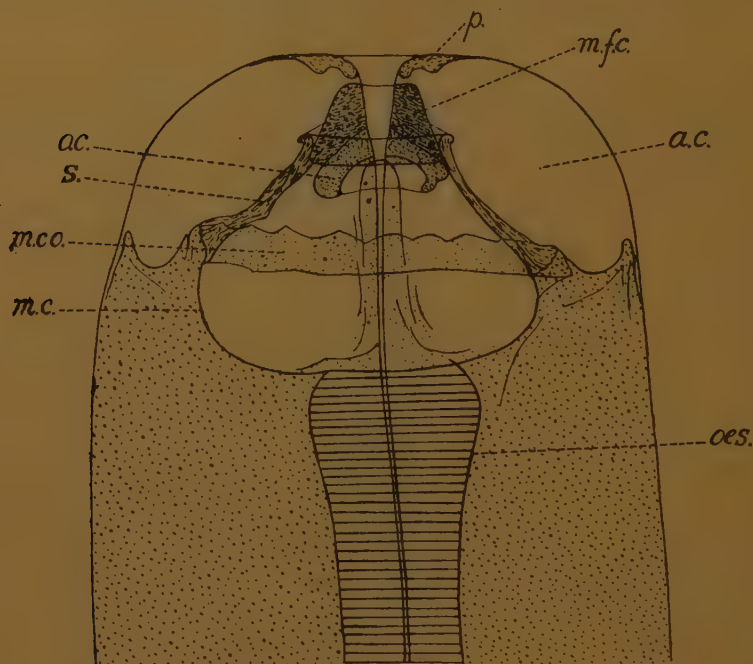


Fig. 4. Anterior extremity of a larva of *S. edentatus*, long 13,7 mm., in which the definite mouth-capsule is formed for the greater part ( $\times 112$ ).

out whether this is a deviation from the normal development or whether we have to do with a different species in this case. It is not in favour of the last hypothesis that these larvae were found under the peritoneum parietale.

The oesophagus of the larva of the fourth stage is slender, just as in the young larva (fig. 1), described above. The maximum length, observed by us, is 1.2 mm. The oesophagus thickens somewhat backwards. The beginning of the mesenteron is broad, the lumen wide. The rectum is short and ends almost terminally. The posterior end of the body is blunt and shows distinct sexual differences (fig. 5). In male as well as in female larvae it is much more obtuse than in the larvae of *S. vulgaris* (cf. IHLE & VAN OORDT, 1924, fig. 1).

In all larvae both enormous excretory cells (cervical glands) are distinctly perceptible. MARTIN (1910, p. 124, fig. I & II) also points



to this fact. The anterior extremity of these cells is situated in front of the middle of the oesophagus, the posterior extremity can extend into the second half of the body. After the moult the excretory cells are still distinctly visible in the young animal; in adult specimens (living in the large intestine) they are much less distinct (IMMINK, 1921, p. 9, pl. I, fig. 1). In larvae of *S. vulgaris*, rendered transparent in creosote, they are not visible.

We have made only a few observations about the development of the gonads. MARTIN (p. 125) communicates that in female larvae of 7 mm. length the gonads are distinctly perceptible. In a female larve of 12 mm. length we have found a well-developed vagina and uteri. However, the vulva is still closed by the larval cuticle. In a male specimen of 12.5 mm. length we also observed the anlage of the ribs of the bursa copulatrix: small nodules, observed also by MARTIN (1910, p. 125).

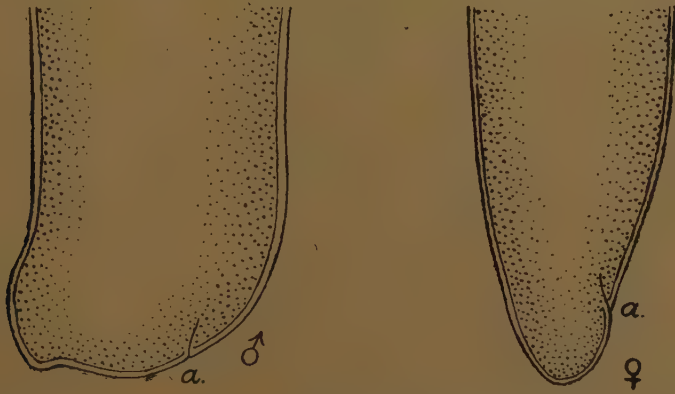


Fig. 5. Posterior extremities of a male larva (long 12,5 mm.) and a female larva (long 11.25 mm.) of *S. edentatus*. ( $\times 85$ ).

According to MARTIN the young animals migrate, after having moulted, from the subserosa of the peritoneum parietale to the radix mesenterii, from which place they creep between the plates of the mesenterium to the large intestine of the horse. It is generally accepted that they form a nodule, while staying in the submucosa. From this nodule they pierce into the gut-cavity. However, we doubt whether the stay in the gut-wall lasts a long time, because we only found young specimens of *S. vulgaris* and never of *S. edentatus* in the numerous nodules investigated.

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#### ABBREVIATIONS.

*a.* = anus.

*a.c.* = anterior cavity.

*ex. c.* = excretory cell.

*m.c.* = mouth-capsule.

*m.c.c.* = mouth-capsule-cavity.

*m.co.* = mouth-collar.

*m.f.c.* = mouth-funnel-collar.

*o.c.* = oesophagus-collar.

*oes.* = oesophagus.

*p.* = mouth-plate.

*s.* = septum.

*Zoological Laboratory of*  
*the School of Veterinary Medicine.*

Utrecht, November 1924.

**Chemistry.** — "*The Molecular Heat of Combustion of Successive Terms of Homologous Series*". By Prof. P. E. VERKADE, H. HARTMAN, and J. COOPS Jr. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of October 25, 1924).

The researches published of late on various sides on the alternation of certain physical and physico-chemical constants of the successive terms of different homologous series of organic compounds render it desirable to make a concise communication here on the results of our determinations of the heat of combustion of a number of dibasic acids of the oxalic acid series. Besides we will set forth our working-programme on the subject of heat of combustion of the normal terms of homologous series, hoping that this sphere of action may be left reserved for us.

This communication is, therefore, intended to give only an indication of the main lines along which our work in this field will be conducted in the future. A fuller discussion of the points mentioned here will be found elsewhere.

Already many years ago the first 9 terms ( $C_2$  to  $C_{10}$ , inclusive) of the oxalic acid series were burned with comparatively great accuracy by STOHMANN and his collaborators<sup>1</sup>). They found that — as is the case in several homologous series — the first and second term (oxalic acid and malonic acid) occupy a particular place, in so far as the heat of combustion of both is very high compared with that of the other terms of the same series. They further found that the molecular heat of combustion of the higher terms (from succinic acid) did not increase by an almost constant amount of 156 to 157 Cal. for every added  $CH_2$ -group — as these investigators had found for some other homologous series, or as they have at least believed they had proved; *it was necessary*<sup>2</sup>) *to distinguish in the series of normal saturated dibasic acids two thermal homologous series, one of which comprises the acids with an even number of*

<sup>1</sup>) STOHMANN, KLEBER and LANGBEIN: Journ. f. prakt. Chem. (2) **40**. 202 (1889); STOHMANN and KLEBER: *ibid.* (2) **45**. 475 (1892).

<sup>2</sup>) Cf. STOHMANN, KLEBER, LANGBEIN and OFFENHAUER: Verhandl. Sächs. Akad. d. Wiss. **45**. 605 (1893).

carbon atoms, the other the acids with an odd number of carbon atoms.

To indicate the place of a compound in a homologous series we shall henceforth introduce the term of "*term number*", analogous to the term of "*atomic number*" introduced elsewhere. An even term is a term with an even term number. It should be borne in mind that such a term contains an odd number of carbon atoms in the series of the dibasic acids considered here, but on the other hand an even number of carbon atoms in the series of the fatty acids.

We have first determined anew the heat of combustion of the acids examined already by STOHMANN c. s., and we have then continued the series to the  $C_{11}$ -acid inclusive, in order to bring out the phenomenon still more clearly. The description of the method of preparation of the acids, of the difficulties met with in the combustion of some of these acids, and of the way in which these difficulties were overcome etc. will be given elsewhere. It may only be mentioned here that it is obvious that of every acid at least two preparations had to be burned, the heats of combustion being based on that of benzoic acid of 6324 cal<sub>15°</sub> per gram (air)<sup>1)</sup> assumed by international agreement.

The following table gives the results obtained by us; the heats

Term-number			Mol. H. of C. in Cal <sub>15°</sub>	$\Delta$ in Cal <sub>15°</sub>	
1	C <sub>2</sub>	oxalic acid	60.2	146.3	
2	C <sub>3</sub>	malonic acid	206.5		
3	C <sub>4</sub>	succinic acid	357.1	150.6	
4	C <sub>5</sub>	glutaric acid	514.9	157.8	
5	C <sub>6</sub>	adipic acid	669.0	154.1	156.0×2
6	C <sub>7</sub>	pimelic acid	827.7	158.7	
7	C <sub>8</sub>	suberic acid	983.4	155.7	157.2×2
8	C <sub>9</sub>	azelaic acid	1141.7	158.3	
9	C <sub>10</sub>	sebacic acid	1297.3	155.6	157.0×2
10	C <sub>11</sub>	nonane dicarboxylic acid	1455.6	158.3	
11	C <sub>12</sub>	decane dicarboxylic acid	1610.7	155.1	156.7×2
12	C <sub>13</sub>	brassylic acid	1768.6	157.9	
					156.3×2

<sup>1)</sup> VERKADE: Chem. Weekblad 19. 389 (1922).



of combustion given apply to an isothermal reaction at a temperature of about 19°.5.

The conclusions at which STOHMANN c.s. had arrived, are confirmed in an indeed striking way by our measurements, which were executed with scrupulous care. Oxalic acid and malonic acid actually occupy an exceptional place: the difference in molecular heat of combustion between these two acids and between this latter acid and succinic acid is considerably smaller than that found between any other two successive terms; this fact need not occupy us now any longer, however. We further see that starting with succinic acid, a great and a small combustion heat increment  $\Delta$  regularly alternate; the mean values of these two increments — to which, for the rest, we do not wish to assign any significance (see below) — are resp. 158.2 and 155.1 Cal<sub>150</sub>. If however, we, regard the even and the odd terms as separate series, we find in the two series but little fluctuating combustion heat increments, the means of which amount resp. to  $2 \times 156.7$  and to  $2 \times 156.7$  Cal<sub>150</sub>. Hence here two thermal homologous series may be spoken of, that of the acids with even term-number, and with odd term-number. One series is shifted about 1.5 Cal<sub>150</sub> with respect to the other.

We wish explicitly to state here that these mean values of the combustion heat increments are given by us merely to elucidate the phenomenon in question, and by no means because we would consider the heat of combustion as an additive quantity, hence the fluctuations in the combustion heat increments as exclusively due to errors of observation. Though in many cases an exceedingly remarkable regularity is observed in the value of the heats of combustion of organic compounds, *it is self-evident that the heat of combustion is without any doubt no additive quantity.*

As yet the series of the normal saturated dibasic acids is the only one in which this phenomenon of the alternation of the combustion heat increments has been observed with certainty. A careful critical examination of the numeric material available in literature has led us to the strong suspicion that a similar alternation of the combustion heat increments is also found at least in the series of *mono-alkylsubstituted malonic acids*, and that this alternation is about of the same order of magnitude. The small number of normal terms, however, of which the heat of combustion has been determined in this case, renders the drawing of a definite conclusion impossible for the present; we intend to undertake the study of this series of acids before long.

Recently GARNER and RANDALL<sup>1)</sup> determined the heat of solidification (heat of crystallisation) with great accuracy for a number of normal terms of the fatty-acid series. Their results are recorded in the subjoined table, which besides gives the most reliable data about the heat of solidification found in the literature for three other acids of the same series (marked \*).

		Mol. heat of solidification	Heat of transition $\alpha \rightarrow \beta$	Mol. heat of solidification of the $\beta$ -form
C <sub>1</sub>	formic acid *	2.52 Cal.		
C <sub>2</sub>	acetic acid *	2.77		
C <sub>8</sub>	octylic acid	5.11		
C <sub>9</sub>	nonylic acid	4.85	1.33 Cal.	6.17 Cal.
C <sub>10</sub>	decylic acid	6.69		
C <sub>11</sub>	undecylic acid	6.00	1.84	7.84
C <sub>12</sub>	lauric acid	8.76		
C <sub>14</sub>	myristic acid *	10.84		

Plotting the molecular heats of solidification in a graphical representation against the term-number (i.e. against the number of carbon

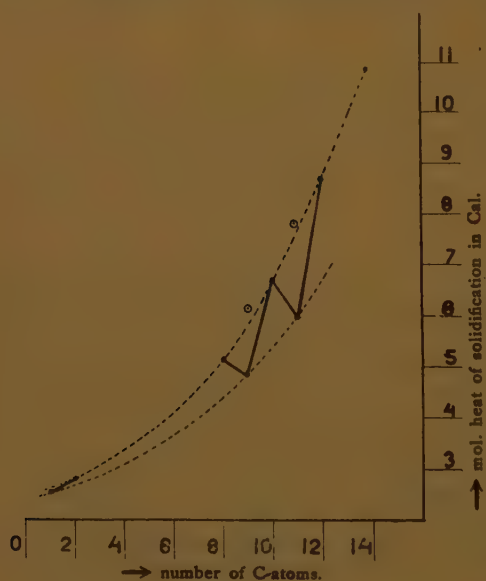


Figure 1.

atoms of the chain), it appears that two continuous curves can be drawn through the points obtained: on one are situated all the terms with even term-numbers, on the other all the terms with odd term-numbers (see fig. 1). Hence the heat of solidification of these acids appears to show, in a very typical way, an alternation in the successive terms of the homologous series. GARNER and RANDALL succeeded in showing in an ingenious way that this alternation is caused by differences in the crystal structure of the even and odd

<sup>1)</sup> Journ. chem. Soc. 125. 881 (1924). We shall discuss this investigation more at length on a later occasion.

terms: for they could prove the existence of two enantiotropic forms of the odd terms in two cases (i.e. for nonylic acid and undecylic acid)<sup>1)</sup> and besides establish that the sum of the heats of transition i.e. the heat liberated in the transition from the  $\alpha$ - into the  $\beta$ -form, and the heat of solidification of the  $\alpha$ -form is about equal to the heat of solidification of the  $\beta$ -form. In the figure the  $\beta$ -forms of the odd series lie pretty well on the line connecting the even terms of the series; they are marked with © in the figure.

The considerations on the way of arrangement of the molecules in the crystals of the even and of the  $\alpha$ - and  $\beta$ -odd forms given by GARNER and RANDALL in connection with their results, may be left undiscussed here, as not bearing directly on the end we have in view.

Now the question arises whether the oscillation of the combustion heat increments found by us in the *crystalline* normal saturated dibasic acids at 19°.5 must be partially or entirely attributed to a different crystal structure of the even and odd terms.

In order to decide this we should have to compare the molecular heats of combustion found for the crystalline acids with those of the supercooled, liquid acids at the same temperature (19°.5). The difference in molecular heat of combustion between a crystalline acid and the same acid in liquid supercooled condition, both heats of reaction measured for an isothermal reaction at the just-mentioned temperature, is not only determined by the molecular heat of solidification ( $s$ ), but also by the difference in specific heat of the acid in the solid and in the supercooled liquid condition ( $v$ )<sup>2)</sup> and by the position of the melting-point ( $t$ ). For an acid of molecular weight  $M$  this difference is:

$$V = s + M v (t - 19.5)$$

in which it may still only be pointed out here that  $v$  can be both positive and negative. If in the case of normal saturated dibasic acids in the liquid state the regular oscillations of the combustion heat increments are to disappear entirely, *the general condition is that both in the series of the even terms and in that of the odd ones the difference  $V$  shall increase from term to term by a constant amount equal for the two series.*

Let us first consider the following special case. In many homolo-

<sup>1)</sup> Cf. TAMMANN: Zeitschr. f. anorg. Chem. **109**, 221 (1923).

<sup>2)</sup> For simplicity a possible variation of the specific heat with the temperature has been left out of account here.

gous series — also in the series in question — the melting-points of the successive terms show likewise a typical oscillation. Besides they present the peculiarity that when we get higher in the series the melting-points approach each other more and more. We may now imagine the theoretical case that a number of successive high terms of a homologous series have all almost the same melting-point; we then consider the isothermal heat of combustion of the solid state and of the liquid state at the temperature of the melting-point. The difference between these two molecular heats of combustion for each term then amounts to:

$$V' = s.$$

If farther we suppose the molecular combustion heat increments for the crystalline substances between an odd term and the next even term to be always 158.2 Cal., and between the latter and the next odd term to be always 155.1 Cal. — i. e. if for a moment we suppose a pure additivity of the heat of combustion, the following interesting relations may be derived.

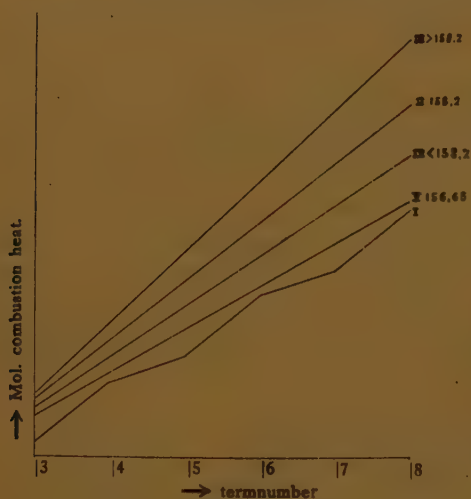


Figure 2.

*A general condition for the total disappearance of the oscillations in the liquid state is that both in the series of the even terms and in that of the odd terms the molecular heat of solidification increases from term to term by a constant amount equal for the two series. When the molecular heats of solidification and the term-numbers are joined in a graphical representation, we get two straight, parallel lines.*

There is now a close relation between the angle of inclination

of these solidification-heat lines, their mutual position, and the value of the combustion heat increment of the substances in the liquid state. A full discussion of this relation will be given elsewhere. Here we will only point out the following conclusions, which can be easily derived by the aid of fig. 2, in which line I diagrammatically represents the course of the heat of combustion of the crystalline substances.

1. If the increment of heat of combustion for the liquid substances is exactly 158.2 Cal. (line II), the heat of solidification of every even term is equal to that of the preceding odd term.



2. If this increment is *greater than 158.2 Cal.* (line III), the heat of solidification of an even term is greater than that of the preceding odd term; if it is *smaller than 158.2 Cal.*, the heat of solidification of the even terms is always smaller than that of the preceding odd term (line IV).

3. If this increment is 156.65 Cal., i. e. exactly the mean of the values of 158.2 and 155.1 Cal., the heat of solidification is constant for all the even and for all the odd terms (line V).

4. A still smaller increment of the heat of combustion for the liquid substances than 156.65 Cal. leads from any term of the homologous series to negative heats of solidification; *hence it is impossible.*

Let us now for a moment return to the general case. Here the same relations are valid, provided the differences  $V$  be substituted for the heats of solidification. This case, too, will be discussed more at length elsewhere.

The slight fluctuations which each of the two series of combustion heat increments of the crystalline acids presents in our case, bring no change at all in the general aspect of these relations. Which of the possibilities 1—3 will occur here, cannot be said with certainty a priori; on the ground of the increment for the  $\text{CH}_2$ -group found in other series of liquid compounds it seems probable that here the combustion heat increment of this group will appear to lie below about 158.2 and above about 156.7 Cal.

The same considerations are valid for the mono-alkylmalonic acids discussed above, if actually the same phenomenon of oscillation should be found to exist in these crystalline acids as in the acids of the oxalic acid series.

Without any doubt the heat of solidification and also the specific heat of the melted (resp. supercooled) acid cannot be determined for most of the dibasic acids of the two series discussed, among others on account of anhydriation, resp. splitting off of carbonic acid during the heating. In the first place we therefore set ourselves the task to determine, by way of expedient, the heat of combustion of series of liquid derivatives of these acids, e.g. of *ethylesters*, and especially of *methylesters*, in order to decide whether, and if so in how far, there still exists an alternation of the combustion heat increments. In some cases the heats of combustion of the solid and the liquid state of the methylesters can be both determined directly by working in an adiabatic calorimetric system at different temperatures, the heats of solidification and the specific heats being

also measurable here. Hence we can form a complete idea of the state of things at least in these few cases. If these liquid derivatives should show an almost constant combustion heat increment, it would have been rendered probable, at least to some extent, by an indirect way that the periodicity of these increments in the crystalline acids is due to differences in the crystalline structure of the even and the odd terms.

It is still quite an open question whether perhaps all homologous series of crystalline compounds show periodicity of the combustion heat increments in a more or less pronounced degree. It is of course by no means a priori necessary then that in all cases — as this is the case with the acids of the oxalic acid series — two unequal, but both almost constant combustion heat increments, regularly alternate. This problem will be investigated by measurements on different series of homologues (preferably such for which also a measurement of the heats of solidification and of the specific heats of the solid and the liquid state is possible) for the particular purpose of ascertaining the constitutive influences, which either produce, or strengthen, resp. weaken these oscillations.

The material of facts concerning the heats of combustion of the normal saturated dibasic acids used in this communication has been collected by the second of us (H.).

*Laboratory of the Dutch Commercial High School.*  
*Rotterdam, Oct. 24, 1924.*

**Histology.** — "*Reversible Gelation as a test for Differences in Permeability of Living Cells.*" By Miss Dr. M. A. VAN HERWERDEN.  
(Communicated by Prof. J. BOEKE).

(Communicated at the meeting of September 27, 1924).

Microscopical examination enables us to recognize in the tail of the living tadpole, thanks to the transparency of the skin, a vivid image of the mesenchyma with bloodvessels and nerve-plexus. When focussing for the epithelial cells we may sometimes distinguish the periphery of the cells, if intercellular spaces and bridges are present <sup>1)</sup>, the *nuclei* of these cells, however, cannot be made out. Now, when placing the larva in a dilute solution of acetic acid of a concentration that does no immediate harm to the animal, we shall see sooner or later a well-defined image of all the epithelial nuclei of the tail. The nucleus is no longer invisible, its contents are granular: a membrane, highly refringent particles and often a less refractive nucleolus are distinguishable. If the karyokinetic process happens to be going on, even chromosomes or a spirema may be observed. The cytoplasm, which at first was transparent, now becomes granular, while sometimes with oil-immersion chondriosomes are observable. The phenomenon begins at the border of the tail, then spreads over the whole tail.

When returning the tadpole to the water, the nuclei will again become invisible, without any injury being done to the animal. The only consequence is an augmented escape of leukocytes from the vessels. This treatment may even be repeated after some hours without endangering the life of the animal. If, however, it is repeated often, at short intervals, this will tell on the cells in the distal portion of the tail, while there is a tendency to extravasation. At long intervals, e. g. half a day, a treatment with dilute acetic acid (0.05—0.075 %) is tolerated unimpairedly. In this simple way structures may be observed in the epithelial cells, which are generally seen only in fixed cells.

This fact, which, in principle, was known already to the early histologists, as RANVIER, would not in itself be worth mentioning, *if the process did not take place in the living animal and were not reversible.*

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<sup>1)</sup> These need not be artefacts, as they appear occasionally in the normal, living tadpole.

That weak acids can indeed penetrate into living animal cells has been demonstrated in 1915, by NEWTON HARVEY by a change of colour of the natural pigment of the *Holothuria Stichopus ananas*<sup>1)</sup>.

In another publication I have set forth that in the tadpole the dilute acetic acid presumably causes a reversible gelation<sup>2)</sup>. There can hardly be question of a precipitation of nucleoproteins through this acetic acid, as is seen in vitro, it being difficult to imagine that these proteins should detach themselves completely for some time from the protoplasm, and directly after the removal of the acid should find their way into it again<sup>3)</sup>. Reversible local changes in hydration of the different protoplasma colloids will probably be responsible for the changes in refraction, which enable us to see cell structures that were invisible before the treatment.

When this modification of the epithelium is again reverted by placing the tadpole in water, and the experiment is repeated soon after, say within an hour, the nuclei will become visible mostly after a much shorter interval than in the first experiment. If, however, the experiment is repeated after several hours only, the tissues will most likely have reverted to their normal state, in consequence of which the time needed for the appearance of the nuclei will be about equal to that of the first experiment. Methylene green added to the acetic acid in a weak concentration, say 0.001 %., only causes a coloration of the nucleus, when the reversibility has been abolished through long-continued acid-treatment. A nucleus occasionally staining within the limits of the reversible reaction, always appears to belong to injured or dead cells. When the larva is returned to the water again, the reversibility of such a nucleus will be observed to have gone.

These experiments confirm in the living animal M. REED NEWTON's recent experience with tissue-cultures of the chicken-embryo outside the organism. Also in her experiments the nucleus was temporarily made visible by weak acids, and after brisk rinsing the tissue could grow further again<sup>4)</sup>.

The mere fact that we are enabled to study parts of one and the same cell of the living animal in different phases is not to be

<sup>1)</sup> Int. Zeitschr. phys. chem. Biologie. Bd. I. 1915, p. 463 (vide HOEBER, Physikal. Chemie der Zellen und Gewebe. 5 Auflage 1924).

<sup>2)</sup> Biol. Centralbl. 1924, vol. 44, p. 579. Zeitschr. f. exp. Zellforschung Bd. I 1925 (in press).

<sup>3)</sup> TSCHERMAK. Allgemeine Physiologie I. 1916, p. 152: exposition of the difference between gelation and precipitation through acids.

<sup>4)</sup> JOHNS HOPKINS Bull. 1923. Vol. 34, p. 373.



overlooked. As to the cytological significance it should be borne in mind that only a limited space of time is available for observation, if the reversibility is to be maintained. My first experiments were made on non-narcotized tadpoles, in order to preclude any other abnormal condition. However, I experienced later on that the addition of a small quantity of water saturated with chlorethane to the dilute acetic acid, say 6 drops to 10 cc. of acetic acid, did no harm, and gave scope for quiet observation. Nevertheless also the non-narcotized tadpole can be kept quiet on an object glass for a few minutes by taking away the superfluous water.

This method may be of some significance for the study of the mitosis and the chromosomes in the living animal. Mrs. LEWIS e.g. has thrice observed a karyokinetic spindle to appear and to disappear again, in the explantation of a chicken-embryo.

In addition to the theoretical significance of the possibility to excite artificially reversible changes in the behaviour of the cell colloids of the living animal without destroying the vital function of the elements concerned, this observation may, I think, also be utilized for the study of permeability.

Some time elapses before the acetic acid can penetrate through the peripheral layer of the protoplasm and render the nuclei visible. This time depends on the concentration of the acid and on the temperature. It may easily be imagined that both influences are distinctly perceptible. So in a solution of 0.075 % acetic acid the reaction occurs sooner than in one of 0.05 %. Likewise while at room-temperature the change in the epithelium appears only after half an hour, at a temperature of 30° it will come forth already within a few minutes (also reversible, provided the tadpole be soon taken out of the solution). In tadpoles from the same aquarium and in about the same stage of development the permeability to acetic acid is about equal for the same temperature.

I expected that the appearance of the nuclei in the epithelium might serve as a test for differences in the permeability evoked by outward circumstances. I tried in this way to investigate whether the exposure of the living tadpole to radium rays modifies the interval before the epithelial nuclei become visible under the microscope.

To my knowledge CH. PACKARD is the only investigator who has demonstrated for living animals (in casu Infusoria) a modification in the permeability after radiation<sup>1)</sup>.

<sup>1)</sup> Biol. Bull. 46. 1924, p. 165.

PACKARD availed himself of the change of colour given by neutral red when passing from an acid to an alkaline-reaction, and thus found that the permeability for ammonia increased with the time of radiation. For the study of permeability to acids neutral red yields no reliable results.

In order to solve the problem whether after radiation it is easier for the acids to penetrate through the peripheral layer of the plasma I exposed tadpoles to radium rays<sup>1)</sup>.

The larva was placed in a small dish with a volume of 1,5 c.c. filled with water and covered by the mica film of the radium preparation (3.1 mgrs of radium-bromide). In long-continued experiments the water was every hour renewed. The control larva was also placed in an equal quantity of water under a single mica plate. When inspecting the tadpole after a radiation of from 1 to 2 hours I observed that the tail proved to have lost its tonus; the circulation was normal or slightly slackened; sometimes there appeared small extravasations in the tail while many leukocytes had left the capillaries (as has also been recorded by GRASNICK<sup>1)</sup>). We verified the invisibility of the epithelial nuclei. Subsequently the two tadpoles were placed in one and the same dish containing 20 c.c. 0,05 or 0,075 % acetic acid. Whereas in the non-radiated larva the acetic acid permeates the epithelial cells and renders the nuclei visible only after about half an hour, resp. after 20 minutes — in the tadpole treated with radium-rays these nuclei manifest themselves over the whole surface already after a few minutes stay of the tadpole in the same dish.

This simple experiment, which, when repeated, always yielded the same results, proves that radium-radiation promotes the permeability to acetic acid. Also in the radiated tadpole the local gelation is reversible so that the experiment may be repeated with the same animal. The tail, however, has become much more sensible to injury than that of the control-larva, and, unless the larva is immediately immersed in a large quantity of water again, after the appearance of the nuclei, there is every chance that the reversibility has come to an end. The tendency to extravasation increases, the flaccid tail has a tendency to shrink into folds. The next day the radiated tadpole may still be distinguished from the normal control larva. In young animals complete recovery sets in later on, which

<sup>1)</sup> In 1917 W. GRASNICK (Archiv f. micr. Anatomie Bd. 90. 1917, p. 1) has radiated the tail of *Axolotl* and *Rana fusca*, but only for the study of histological details.

recovery is sometimes attended with a morbid growth of epithelium at the border of the tail.

According to PACKARD it is the slow  $\beta$ -rays, *not* the quick  $\beta$ -rays or the  $\gamma$ -rays that promote in *Paramaecium* the permeability to alkali. In PACKARD's experiments the action of the radium failed to appear on filtration of the radium-rays through a lead-filter of 2 mm. thickness.

In order to ascertain whether by covering the radium preparation by means of such a lead-filter the larva kept an unchanged permeability to acetic acid, — I put the tadpole in a small dish filled with water under a thin mica film, which was covered by a leaden platelet of 2 mm. diameter, on which the radium preparation was laid. In these cases the radiation was continued for 2 or 3 hours, and every hour the water was renewed. The mica film served to protect the tadpole against the lead. The tail of all the tadpoles treated in this way displayed properties similar to those of the tadpoles radiated without a lead filter. So I can't hold the  $\beta$ -rays responsible for the augmented permeability to acetic acid. Of course the  $\alpha$ -rays cannot be held responsible either, as we know that they are already held back by the mica window of the radium-mantle.

Concerning the permeability of the epithelium of the larval tail to alkali I have made, with neutral red as a reagent, a series of comparative experiments with radiated and with non-radiated tadpoles, to investigate whether the so easily demonstrable increase of permeability to acids also holds with regard to alkali. The secretion-granules in the glandular cells of the skin (LEYDIG's cells) are rapidly stained in a solution of 0,005 % neutral red. After some time also the mesenchyme is seen to contain pinkish granules, at first in the cells lining the lymphatics, afterwards also in the other mesenchymal cells. When two larvae, of which the one has been radiated for one hour in the manner described (without a lead-filter), and the other serves for a control-experiment, are both transferred from the neutral red into a faintly alkaline medium, which e.g. contains one drop of ammonia liquida to 100 c.c. of water, we shall, after a short time observe here and there red granules in the mesenchyme giving place to light yellow ones through a change of the reaction, caused by the penetration of the alkali into the undamaged tail. However, this change of reaction in the mesenchyme does not at all occur everywhere at the same time, which probably depends on the local reaction of the tissue but which renders it very difficult to form a proper estimate. Neither did I succeed, therefore, with weaker concentrations of the ammonia solution to demonstrate a



distinct difference in permeability between radiated, and non-radiated tadpoles. In contradistinction to the change of colour in the mesenchyme it will be seen that with the above concentration LEYDIG's cells firmly retain the red stain in non-radiated as well as in radiated larvae. In two experiments a concentration of 4 drops of ammonia to 100 c.c. of water was needed to ensure a change from red to yellow in these latter cells. This no doubt implies that these glandular cells have their own acid reaction.

After long-continued rinsing in a large quantity of water the same radiated, and non-radiated tadpoles, used for the above alkali experiments, are now placed in a dish with 0,075 % acetic acid. It then appears that there is a considerable difference in the permeability to acetic acid, while with alkali there was only very little and hardly demonstrable difference. Just as in the experiments, already described, the epithelial nuclei (not visible before) make their appearance in the radium-larva almost immediately, while on the other hand in the control-larva they appear 15 minutes later.

Every one who carries out these experiments will experience that the acetic acid test yields in the tadpole a more decisive proof of the increased permeability after the radium treatment than the neutral red-alkali test.

As to the permeability of the epithelium to different dyes no difference could be made out between radiated, and non-radiated larvae (neutral red, methylene blue, and Nile blue sulphate) the time of radiation being the same that has proved distinctly to increase the permeability to acetic acid.

Judging from the recent bibliographic manual of TSCHERMAK <sup>1)</sup> on general physiology little is known about the effect of radium-rays on the permeability in the living cell. The increased permeability to acetic acid caused by radiation now appears to be readily demonstrable through local reversible gelation, which may be evoked in the epithelium of the living tadpoles. Presumably the peripheral layer of the plasma has been modified by the radium rays, in consequence of which the *H*-ions are sooner admitted to the interior of the cell. The reversibility of the reaction proves at the same time that the increased permeability is in this case not to be attributed to the death of the cell.

Through lack of the living material in the latter part of the summer, I am not in a position to test this phenomenon for other acids.

<sup>1)</sup> Allgemeine Physiologie. Bd. 1. 1916. and Bd. 2. 1924. Springer Berlin.



**Chemistry.** — "*The Relation between Velocity of Diffusion, Viscosity, and external Pressure*". By Prof. ERNST COHEN and Dr. H. R. BRUNS.

(Communicated at the meeting of September 27, 1924).

*Introduction.*

The answer to the question, as to what relation there is between the viscosity of the medium, in which diffusion proceeds, and the velocity with which it takes place, is of great importance for our conceptions about the mechanism of the friction which the molecules of a liquid experience during their movement.

In a former paper <sup>1)</sup> we have summarized the older investigations on this subject. How the velocity of diffusion depends on the viscosity can be investigated by determining the changes which the two values undergo during a change of temperature. It was found that the velocity of diffusion is inversely proportional to the viscosity, not only when molecules with great diameter diffuse (this result was to be expected as a consequence of STOKES's law) but also — with relatively small discrepancies — when the molecules of the diffusing substance and the diffusion medium are of the same size.

Now the question arises: does this relation hold, if another variable of state is taken as independent variable? As, according to our investigations, it was possible to measure velocities of diffusion accurately, also at high pressure, we may take now external pressure as independent variable.<sup>2)</sup>

So we had to determine the influence of pressure on the viscosity of the medium used, in a case where the influence of pressure on the velocity of diffusion is known.

As in our investigation <sup>2)</sup> described recently we had studied the influence of pressure in the interval 1—1500 atm. on the velocity of diffusion of cadmium in mercury (at 20°.0 C.), we have now investigated the influence of pressure on the viscosity of mercury, at the same temperature. This paper gives a description of this investigation and of the results obtained.

<sup>1)</sup> Zeitschr. f. physik. Chemie **103**, 404 (1923).

<sup>2)</sup> These Proc. **27**, p. 555 (1924); Zeitschr. f. physik. Chemie **109**, 422 (1924).

*Principle of the method.*

1. The viscosity (at 1 and at 1500 Atm.) was measured with a viscosimeter of the type OSTWALD. The difficulty of such measurements under pressure lies in the fact that the liquid must not flow through the capillary until the apparatus in the pressure bomb has had ample time to assume the desired temperature and pressure.

Moreover it must be possible to determine, outside the bomb, the time necessary for the flowing of a definite quantity of liquid.

2. We have been able to carry this out by the following device: The two "bulbs" *B* and *C* of the viscosimeter, (see Fig. 1), were as much as possible identical as regards form and capacity. In order to prevent the mercury, immediately after filling, to flow through the capillary (before the apparatus in the bomb had assumed the correct temperature and pressure) the upper "bulb" *A* was hermetically closed with the lid *K*. The mercury could not begin to flow before this lid had been opened mechanically. This was brought about by melting, with an electric current, a very thin iron wire which pressed the lid tightly down on the opening at the top of the upper "bulb" *A*. Then a spring opened this lid automatically. The moments when the mercury began to enter the lower "bulb" *C*, and when it was completely filled with mercury, were determined by means of platinum contacts. These contacts were in a circuit, in which (outside the bomb) a storage cell, a resistance, and a sensitive galvanometer had been connected.

*The Apparatus used.*

3. The viscosimeter (Fig. 1) is in a glass vessel *R* which during the experiments was completely filled with water; the viscosimeter itself, in so far as it is not filled with mercury, also contains water. In our figure the condition is represented when the apparatus is ready for an experiment, so when it is going to be put in the pressure bomb, *B* and *C* are the two "bulbs", mentioned already in par. 2, which are as much as possible identical as regards volume and shape. The lid *K* (brass) is closed; it is kept pressed down by means of the very thin iron wire *J*, which at its upper end is wound round the button *M* of the lid, and which carries a hollow metal cylinder *E* at its lower end. In this cylinder is a spiral, which keeps *J* stretched, because it presses against a plate fixed to the lower end of *J*. This plate just fits in the metal cylinder.

The upper part *A* of the viscosimeter is firmly enclosed (clamped with screws) by an ebonite cylinder *O* (in Fig. 1 this cylinder is drawn separately on the right hand) which fits exactly into the

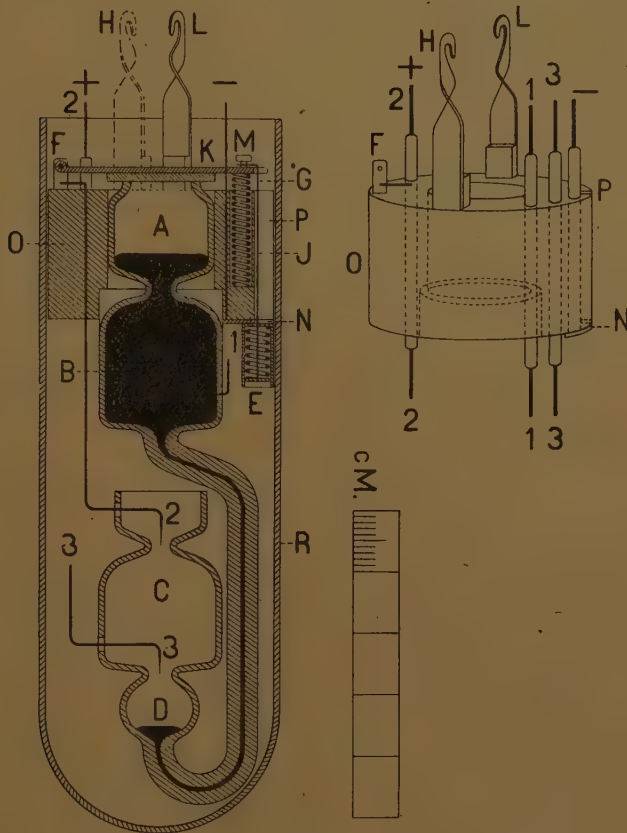


Fig. 1.

glass cylinder *R*, and which for this reason keeps the viscosimeter in that cylinder (and consequently also in the pressure bomb) always in the same position. The external diameter of the cylinder which fitted precisely in the cavity of the bomb, was 3,9 cm.

In the ebonite cylinder, along the side, is a groove *P*, through which runs the wire *J*. The bottom of the lid *K* is covered with a layer of very elastic indiarubber, thus ensuring hermetic closing; the whole lid can turn on the hinge *F*. The edge of the tube *A* at the top is ground smooth.

The spiral *G*, which rests in a cylindrical cavity of *O*, forces open the lid as soon as it is no longer kept down by the iron wire *J*. This is brought about by melting the wire, in a way which will be described later on.

The spiral  $G$  is much weaker than the spiral  $E$ .

The hooks  $H$  and  $L$ , fastened to the ebonite block, carry the whole apparatus, which can be hung up at the steel lid of the pressure bomb, before being let down into the cavity of the bomb. The glass vessel  $R$  then rests on the conical walls of the bomb, so that the whole apparatus is firmly fixed.

The platinum wires 1, 2 and 3 (0,3 mm. thick) have been melted into the wall of the viscosimeter with enamel glass. Wire 2 is in electrical contact with the lid  $K$ . The wires marked + and —, enable us to send a strong current (220 Volt) through the wire, in order to melt it.

The following are the dimensions of the apparatus: Diameter of the "bulbs"  $B$  and  $C$  2 cm. Capacity of  $B$  and  $C$  about 4 cm<sup>3</sup>. Diameter of the capillary 0,2 mm. Length of the capillary 7,5 cm.

Fig. 2 shows diagrammatically the electrical connections of the whole apparatus.

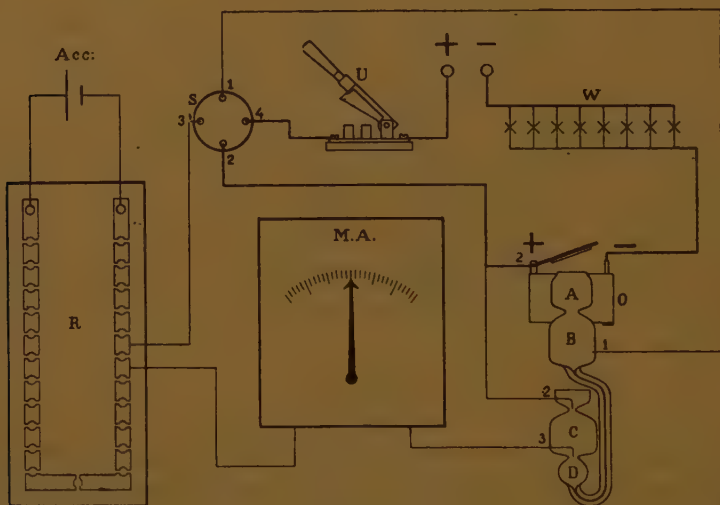


Fig. 2.

$R$  is a resistance box,  $S$  a switch,  $M. A.$  is a milliammeter,  $W$  a lamp resistance,  $U$  is a high current key.

### Measurements.

4. Before *every* measurement of the time of flow of the mercury through the capillary, the apparatus was cleaned anew, first with fuming nitric acid, to remove drops of mercury that had eventually remained behind, then with twice distilled water, alcohol and ben-



zene. This last named substance was removed by evaporation, while air was being sucked through during mild heating. Now a certain definite quantity of mercury (the same in all the experiments, also in those under high pressure) is weighed (65.921 grs) and put into the viscosimeter, so that *B*, and part of *A* are filled with it. By applying a small pressure mercury is allowed to flow into the capillary, until the little bulb *D* is filled. When this is done, water (boiled and cooled in vacuo) is put into the bulb *C* by means of a pipette. The mercury is sucked back by a Bunsen filter pump, until it has the position as indicated in the diagram, so that *D* is now filled with water. The smooth glass edge of *A* is greased with vaseline, and likewise but very thinly the bottom of the indiarubber, covering the lid. Then the bulb *A* is filled up with water.

Now the whole viscosimeter is submerged in distilled water, and then the lid *K* is firmly pressed down with a finger. Subsequently the apparatus is taken out of the water. The iron wire *J* must now be adjusted. This iron wire has already been fitted to the metal plate above mentioned, and to the metal cylinder with spiral. The wire is shoved through a narrow slit in the plate *N*, tightly drawn upward, so that the spiral is stretched, and the end is tightly wound a few turns round the knob *M*. Then the finger is carefully taken off the lid. The viscosimeter is now hung at the lid of the pressure bomb, the ends of the conducting wires 1, 2, 3, and — are soldered to the four wires which run through the stopper of the bomb (Fig. 1), the bulb *C* is completely filled with boiled water by means of a thin pipette, and the slit *P* is filled with vaseline (the reason for this is given below). Finally the vessel *R* is completely filled up with boiled water, *R* is placed round the viscosimeter, and the whole apparatus is let down into the pressure bomb (which has been filled with oil beforehand), and the bomb is closed.

5. The temperature and pressure regulations, as well as the calibration of the manometer, were arranged in the same way as was described in our paper on the influence of pressure on the velocity of diffusion of metals in mercury <sup>1)</sup>. All measurements were carried out at 20°.0 C. At 1 atm. as well as at 1500 atm. pressure they were begun only when the whole apparatus (under pressure after the exchange of the heat of compression) had been kept during four hours or longer at the desired temperature and pressure.

6. The procedure was as follows: Points 2 and 4 of the switch *S* are connected. When *U* is pressed down the strong current is

<sup>1)</sup> These Proceedings 27, p. 555 (1924); Zeitsch. f. physik. Chemie 109, 422 (1924).

sent through the iron wire *J*, and melts it. The lid *K* opens and the mercury begins to flow through the capillary to the "bulb" *C*. Meanwhile the connection 2—4 is switched off, and 1 is connected with 3. In the resistance box *R* the connections are such, that only a small part (f.i.  $\frac{1}{10}$ ) of the E.M.F. of the accumulator is used as source of current, to cause a deflection of the milliammeter. As soon as the flowing mercury reaches the contact 3 (then the circuit *Acc.—R—MA—3—1—S—R—Acc.* is closed) the needle of the M.A. deflects. This moment is noted down. Then in the switch *S* the connection 1—3 is broken and 2 is connected up with 3. As soon as the "bulb" *C* is completely filled with mercury, the circuit *Acc.—R—MA—3—2—S—R—Acc.* is connected up by the mercury in the viscosimeter, and the needle is seen to deflect again. This moment is again noted down. The difference between the two moments noted down is the time of flow wanted. Now the viscosimeter is taken out of the bomb, and has got ready for another experiment.

#### *Remarks.*

*a.* The two "bulbs" *B* and *C* were as closely as possible similar in shape and capacity, in order to eliminate as much as possible the influence of pressure on the surface tension of the mercury, and consequently on the form of the menisci, and so on the mean effective pressure during the flow of the mercury.

*b.* The cylindrical "bulbs" *B* and *C* were rounded off at the top, so as to prevent water bubbles to attach to the wall (this happened at first when the form was cylindrical), which apparently reduced the time of flow of the mercury to a great extent. The shape was not quite spherical in order to obviate the difficulties which would ensue by the spherical form, in fixing the platinum contacts (obliquely).

*c.* The current used for melting the iron wire *J* (diam. 0.15 mm.) was 10 Amp. It was impossible to melt the wire when it was surrounded by water, not even when a stronger current was used. It became possible when it was surrounded by less conductive substances, f.i. oil. Therefore the slit *P* was filled with vaseline.

*d.* Originally we had melted wire *l* into the bulb *D*. Then a crack was caused in *D*, whenever the pressure was applied, probably in consequence of tension in the strongly bent glass. When we had put *l* in *B* the difficulty was overcome.

*e.* The platinum contacts are fixed in *C* and not in *B*, because making contact between mercury and platinum is much more nicely reproduced than breaking it.

*f.* All the liquids used for washing were twice filtered in order to prevent suspended particles getting into the capillary. Benzene was used instead of ether to avoid precipitation of moisture when evaporation was too rapid.

*g.* The water with which the viscosimeter and the vessel *R* were filled, had previously been boiled, and cooled in vacuo, because it was seen that, when the apparatus had been in the bomb for a long time at 20° C. and at 1 atm. air bubbles had formed in *C*, which clung to the wall at the top and apparently reduced the time of flow.

*h.* The dimensions of the apparatus were purposely chosen to render the time of flow very long, viz. about 50 min. This was the reason that errors in the measurement of time (for which an accurate, controlled stopwatch, with division up to  $\frac{1}{5}$  second, was used) were reduced to a minimum.

*i.* The column of water in *A*, over the mercury, was so high, that even during the highest pressure, the oil of the bomb, which surrounded the whole apparatus, could not enter into the "bulb" *A*.

*j.* The diameter and length of the capillary, as well as the (average) height of the mercury, were chosen in such a manner (in connection with the dimensions of the pressure bomb) that the flow in the capillary satisfied POISEUILLE's law, if, at least, we may\* assume that the equation given for water by GRÜNEISEN, also holds for other liquids, even for mercury with its great density. In this case we may write <sup>1)</sup>:

$$\omega_{0.001} = 6.6 \times 10^{-6} \frac{\eta}{ds} \left( \frac{l}{d} - 4.5 \right)^{2.08}.$$

As  $d = 0.019$  cm. (determined by weighing with mercury) and  $l = 7.6$  cm. while  $\omega = 1.5$  and  $s = 13.55$

$$\omega_{0.001} = 5.1 \frac{\text{cm.}}{\text{sec.}},$$

while the actual velocity of flow, calculated according to the formula of POISEUILLE is:

$$\omega = \frac{V}{\pi r^2 t} = 4.3 \frac{\text{cm.}}{\text{sec.}}$$

#### *Calculation of the measurements.*

In order to determine, how the relative viscosity can be calculated from the times of flow measured, we shall consider which values

<sup>1)</sup> See COHEN and BRUINS. *Zeitschr. f. physik. Chemie* **103**, 404 (1924); specially §§ 42-49.

in the formula of POISEUILLE undergo a modification, when the external pressure is modified.

This formula is:

$$\eta = \frac{\pi r^4}{8 l V} p t.$$

Here  $\eta$  is the absolute viscosity;

$r$  is the radius of the capillary;

$l$  is the length of the capillary;

$V$  is the volume of liquid flowed through;

$p$  is the pressure under which the liquid flows out;

$t$  is the time of flow.

As we want to determine the relative viscosity only at 1500 atm. with respect to the relative viscosity at 1 atm., the question is to determine:

$$\frac{\eta_{1500}}{\eta_1} = \frac{\left(\frac{r^4}{lV}\right)_{1500} \cdot p_{1500} \cdot t_{1500}}{\left(\frac{r^4}{lV}\right)_1 \cdot p_1 \cdot t_1}.$$

As  $r^4$  and  $lV$  are of the same dimension  $\frac{\left(\frac{r^4}{lV}\right)_{1500}}{\left(\frac{r^4}{lV}\right)_1} = 1.$

So we find

$$\frac{\eta_{1500}}{\eta_1} = \frac{p_{1500}}{p_1} \cdot \frac{t_{1500}}{t_1}.$$

Here  $p$  is the mean hydrostatic pressure of the column of mercury in the viscosimeter, less the pressure of an equally high column of water, because the flowing of the mercury takes place in a vessel submerged in water:

Let:

$h$  be the mean height of the column of mercury ( $= 4.2$  cm.)

$s_{Hg}$  the density of mercury at the temperature of the experiment (20°.0 C.)

$s_{H_2O}$  the density of water at the temperature of the experiment (20°.0 C.),

then:

$$p = hg (s_{Hg} - s_{H_2O}),$$

in which  $g$  is the acceleration of gravity.



We then find:

$$\frac{\eta_{1500}}{\eta_1} = \frac{h_{1500} (s_{Hg} - s_{H_2O})_{1500}}{h_1 (s_{Hg} - s_{H_2O})_1} \cdot \frac{t_{1500}}{t_1}$$

The value  $\frac{h_{1500}}{h_1}$  can be calculated with the compressibility of mercury, and the mean area of the cross section of the "bulbs" *B* and *C*. For, the volume *V* of the mercury diminishes in consequence of the external pressure with a volume  $\Delta V$  equal to the product of the external pressure, the volume of mercury, and its apparent coefficient of compressibility  $\beta'$  in glass.

The decrease of the mean height of pressure is:

$$\frac{\Delta V}{\text{mean area}}$$

Now:

$$V = \frac{65.921}{13.55} \text{ cc.} = 4.86 \text{ cc.}$$

$$\beta' = 1.7 \times 10^{-6}; \beta_{Hg} = 4 \times 10^{-6}; \beta_{glass} = 2.3 \times 10^{-6}.$$

$$\Delta V = 1500 \times 1.7 \times 10^{-6} \times 4.86 = 12.4 \times 10^{-3} \text{ cc.}$$

As the diameter of the "bulbs" was about 2 cm. we suppose the mean area to be = 3.14, so:

$$\Delta h = -\frac{12.4 \times 10^{-3}}{3.14} = -0.004 \text{ cm} \quad ; \quad h = 4.2 \text{ cm.}$$

then

$$\frac{h_{1500}}{h_1} = 0.999.$$

At 1 atm. is  $s_{Hg} = 13.55$ ; At 1500 atm. is  $s_{Hg} = 13.55 \times 1.006 = 13.63$ .

„ 1 „ „  $s_{H_2O} = 0.998$ ; At 1500 atm. is  $s_{H_2O} = 0.998 \times 1.057 = 1.055$ .

Then:

$$\frac{(s_{Hg} - s_{H_2O})_{1500}}{(s_{Hg} - s_{H_2O})_1} = \frac{12.575}{12.552} = 1.002.$$

So we find:

$$\frac{\eta_{1500}}{\eta_1} = 0.999 \times 1.002 \frac{t_{1500}}{t_1} = 1.001 \frac{t_{1500}}{t_1}.$$

### *Results of the Measurements.*

9. In Table 1 the results of the measurements at 1 atm. and 1500 atm. (Temp. 20° 0 C.) have been recorded.

TABLE 1.  
Temperature 20°.0 C.

1 Atmosphere		1500 Atmospheres	
Number of the experiment	Time of flow	Number of the experiment	Time of flow
1	52 min. 10.8 sec.	8	54 min. 38.8 sec.
2	52 " 9.0 "	9	54 " 38.6 "
3	52 " 18.3 "	10	54 " 40.2 "
4	52 " 10.6 "	11	54 " 39.2 "
5	52 " 10.8 "	12	54 " 35.0 "
6	52 " 8.2 "	13	54 " 34.0 "
7	52 " 12.2 "	14	54 " 38.2 "
Mean 52 min. 11.4 sec.		Mean 54 min. 37.7 sec.	

We find  $\frac{t_{1500}}{t_1} = 1.047$ , then

$$\frac{\eta_{1500}}{\eta_1} = 1.048.$$

### Conclusions.

10. Previously we have found that the velocity of diffusion of cadmium in mercury 20°.0 C. is:

$$\text{At 1 atm. } D_1 = 1.520 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$$

$$\text{At 1500 atm. } D_{1500} = 1.446 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$$

$$\frac{D_1}{D_{1500}} = 1.051.$$

Within the accuracy of the measurements of the velocity of diffusion we find therefore  $D_1 \eta_1 = D_{1500} \eta_{1500}$  or in words: The product of the velocity of diffusion and viscosity is constant, independent of the external pressure.

### SUMMARY.

A method was devised which enables us to carry out accurate viscosity determinations also at high pressure. With this method

we studied the influence of external pressure on the viscosity of mercury (at  $20^{\circ}\text{C.}$ ). This viscosity is increased 4,8% by a pressure of 1500 atm. As the velocity of diffusion of a metal in mercury decreases 5% in the same circumstances it follows that: The product of velocity of diffusion and viscosity is constant, independent of the external pressure.

VAN 'T HOFF Laboratory.

*Utrecht*, September 1924.

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**Physics.** — "*The Removal of Errors Caused by Irregularities in the Registering Apparatus in Self-Registering Micro-Photometers.*" By W. M. KOK and Prof. P. ZEEMAN.

(Communicated at the meeting of October 25, 1924).

In the photographic diagrams made with a self-registering micro-photometer (e. g. that of MOLL), the position of the spectrum lines is determined by measuring the distance between a top and a fixed ordinate, and multiplying it by the magnifying factor determined separately. In the case of symmetrical distribution of the light intensities symmetrically situated points of the intensity curves will probably be chosen instead of the top.

It should, however, be borne in mind that in all this it is tacitly assumed that the coupling between the original photographic plate and the paper on which the photographic diagram is projected, is flawless, and that it is overlooked that the paper may have been transformed during the development.

It is possible to make a very perfect screw for the slide, which works the slide with the photographic negative. But technically it is a very difficult problem to construct with the same accuracy the toothed- and the worm wheels which determine the coupling with the registering cylinder.

A very simple construction renders it possible automatically to register at the same time a scale division which eliminates all the difficulties described.

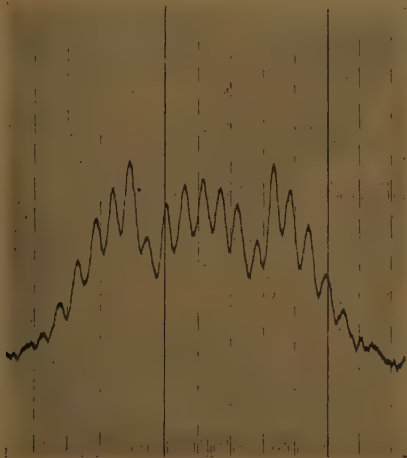
A disc, 33 cm. in diameter, slit radially 2 cm. deep at fifty places — every tenth incision of double the breadth, the fiftieth of four times the breadth — is mounted on the axis working the slide with the negative, the thread of which is assumed to have been cut very accurately.

An auto-lamp (in a tube with slit, 8 Volts 25 N. C.) is placed behind the disc, a lens (10+) is placed before it. The light of the lamp falls on a narrow mirror, mounted on the wall beside the galvanometer ( $\pm 120$  cm. before the photometer). Via the mirror, the lens throws a greatly magnified image of the edge with slits on the front of the registering box. Every time that a slit of the disc passes the light slit of the lamp, the slit of the box is illuminated for a



moment; then a line is drawn on the bromide paper, the tenth line is somewhat thicker, the fiftieth is still heavier.

If the galvanometer and the lamp illuminating the disc can be adjusted separately with a resistance at any tension between 4 and 8 Volts, scale and curve can be obtained of any thickness required; even of the sharpness of a hair, if the cylinder lens of the registering box is very good and accurately adjusted, and when it is covered except for the slit of  $\pm 1$  mm.



If the speed of the micrometer screw is 1 mm., if the paper runs 40 mm., the negative 1 mm. per minute, the lines on the paper will be at a distance of 0.8 mm.;

this distance is the most convenient one for the eye; it corresponds with 20 microns on the gelatine plate.

If the scale division is very fine, it does not interfere with the determination of a top. The accuracy of reading may be reckoned to have become five times greater by this procedure. The method is particularly suitable for the comparison of two curves, which are photographed under each other. If care is taken that the arrangement for corresponding spectrum lines has almost the same position, the second not photographed scale may be assumed to coincide with the first.

As appeared to us later, the method described bears a close resemblance to a procedure due to S. GARTEN to register times on a diagram, which is well known to physiologists. In the literature we have, however, found nowhere mentioned the combination described here for removing errors in the registering apparatus in a microphotometer.

A diagram of the chromium line 4254 in a magnetic field, which contains the line system discussed here, may serve as illustration of the method. The chromium line in question is split up into  $3 \times 7 = 21$  components by a magnetic field, and was photographed by Mr. J. VAN DER MARK in the laboratory at Amsterdam. It was already measured by HILDE GIESELER<sup>1)</sup> and has as symbol  $4_{13}^7 - 4_{22}^7 = 4254,503$ .

<sup>1)</sup> H. GIESELER. ZS. f. Physik 22, 228, 1924.

**Chemistry.** — "*Lyophilic Colloids and POISEUILLE's Law*". By Prof.  
H. R. KRUYT and CONMAR ROBINSON, A.I.C., A.R.C.Sc.I.

(Communicated at the meeting of October 25, 1924).

1. In recent years there has been much controversy as to whether lyophilic sols have a real viscosity in accordance with POISEUILLE's law or whether they possess elastic properties similar to solids. HATSCHEK<sup>1)</sup> is inclined to ascribe elastic properties to these sols; ROTHLIN<sup>2)</sup> who carried out viscosity measurements after the manner of HESS, divides colloids into two groups, those which show elastic properties and those which do not. FREUNDLICH and SCHALEK<sup>3)</sup> find that some sols exhibit elasticity while others do not. WO. OSTWALD<sup>4)</sup> some years ago expressed a similar opinion when dealing with the hysteresis phenomena which these sols often exhibit.

H. G. BUNGENBERG DE JONG<sup>5)</sup> has criticised much of this work on the grounds that the measurements were carried out on sols in which gelation had already commenced. Agar solutions below 40° C. and gelatin solutions below about 30° C. show gelation phenomena even at low concentrations which will not set to solid gels. The experiments of BACHMANN<sup>6)</sup> have plainly shown that even in these dilute solutions gelation coagula are present and it is obvious that these may be accompanied by elastic properties. DE JONG showed that a 1/7 % agar sol followed POISEUILLE's law exactly at 40° C., while on the other hand ROTHLIN has shown that at 27° C. a 1/4 % sol possessed elasticity. FREUNDLICH has recently confirmed DE JONG's result.

2. In the paper of FREUNDLICH and SCHALEK already referred to, it is once more stated that a number of sols show deviations from POISEUILLE's law. They again investigated the viscosity of a gelatin sol, using a 1/4 % solution at 23° C. We contend that this deviation

<sup>1)</sup> Koll. Zeit. **8**, 34 (1911); **12**, 238 and **13**, 88 (1913).

<sup>2)</sup> Biochem. Zeit. **98**, 34 (1919).

<sup>3)</sup> Z. physik. Chem. **108**, 153 (1924).

<sup>4)</sup> Trans. Faraday Soc. **9** (1913), Koll. Zeit. **12**, 213 (1913).

<sup>5)</sup> Rec. Trav. Chim. **42**, 1 (1923).

<sup>6)</sup> Z. anorg. Chem. **73**, 125 (1911); **79**, 202 (1912).

can be altogether accounted for by the fact that gelation had already set in, since DE JONG<sup>1)</sup> has established the fact that with gelatin at 40° C., POISSEUILLE's law is followed exactly.

FREUNDLICH and SCHALEK and also SZEGVARI<sup>2)</sup> maintain that these investigations should not be carried out with the OSTWALD viscometer, but with either the COUETTE or the HESS viscometer. Whether this contention is correct or not, we shall see in the following paragraph; but so that there should be no doubt we have used the HESS apparatus for investigating gelatin sols at temperatures above and below the temperature where gelation commences. For this purpose certain modifications of the HESS apparatus had to be introduced.

Firstly it had to be possible to bring the apparatus conveniently to temperatures higher than that of the room and to maintain such temperatures for long periods. The two capillaries were therefore placed in a long narrow trough through which water from a thermostat could be circulated.

Further, the liquid whose viscosity is to be measured must be introduced into the apparatus without being allowed to cool below the temperature of the experiment. For this purpose a *T*-piece was attached to the end of the tube leading to the capillary. The lower end of this *T*-piece was made to pass through the bottom of the trough and was fitted with a ground glass stopper. (See fig. 1).

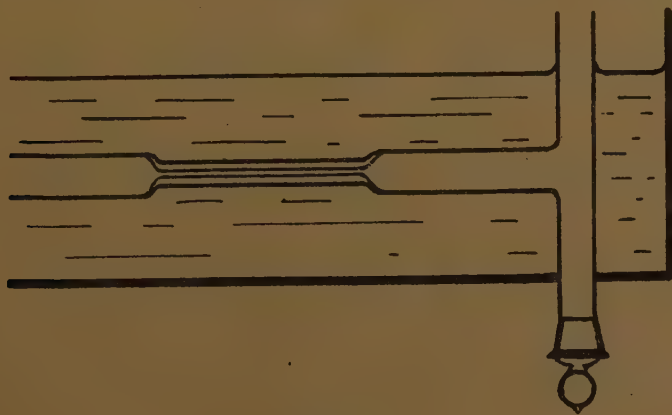


Fig. 1.

The perpendicular tube of the *T*-piece was filled with the solution, the necessary quantity of liquid drawn through the capillary and the remainder allowed to run out by removing the glass stopper.

<sup>1)</sup> Rec. Trav. Chim. **43**, 35 (1924).

<sup>2)</sup> Z. f. physik. Chem. **108**, 175 (1924).

The reading of the graduated tubes was facilitated by placing a mirror scale under the tubes, and a capillary was chosen of such dimensions as to give with the pressures used in the experiments an error of less than 0.1 % as shown by GRÜNEISEN's<sup>1)</sup> formula.

In the following table are the results of our experiments with 0.25 % Gelatin sol.

Temperature	Pressures (mm. of Hg)	T <sub>s</sub> /T <sub>w</sub>
40°	60	1.13 <sup>0</sup>
	30	1.13 <sup>2</sup>
	10	1.13 <sup>1</sup>
30°	60	1.15 <sup>4</sup>
	30	1.15 <sup>8</sup>
	10	1.15 <sup>6</sup>
23°	60	1.47 <sup>6</sup>
	40	1.49 <sup>1</sup>
	20	1.50 <sup>2</sup>
	10	1.51 <sup>1</sup>

Here we see that the Gelatin sol follows POISEUILLE's law exactly at 40° C. and 30° C., while at 23° C. the expected deviations appear.

3. HESS, FREUNDLICH and SCHALEK, and SZEGVARI have condemned the use of the OSTWALD viscometer for the viscosity measurements of these systems. Here, however, we think one should first consider with what purpose the experiment is to be carried out.

When elastic properties are exhibited as for example in the case of old  $V_2O_5$ -sols, then one obtains a relationship between viscosity and pressure as shown in fig. 2. Further SZEGVARI has shown theoretically that the following general formula holds when elastic properties are present:

$$w = \frac{\eta}{G} + \eta$$

where  $w$  is a quantity proportional to the amount of liquid which

<sup>1)</sup> Wiss. Abh. Phys. Techn. Reichsanst. 4, 151 (1905).



flows through in unit time,  $\vartheta$  the liquid elasticity,  $G$  the fall of velocity and  $\eta$  the actual viscosity. This equation is that of an hyperbola with the ordinate as an asymptote.

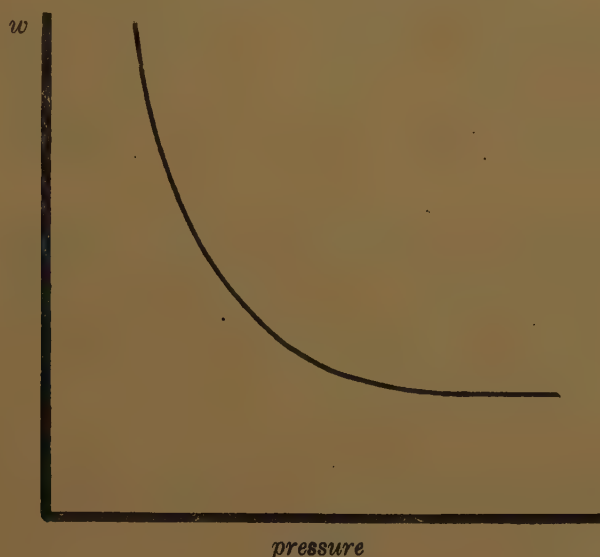


Fig. 2.

From this one sees that the term  $\frac{\vartheta}{G}$  plays a smaller and smaller rôle the greater the fall in velocity, that is to say the greater the pressure employed. An apparatus in which the measurements are carried out at high velocities of flow, that is to say, at high pressures will thus give results which approximate very closely to the actual viscosity of the liquid. But the question whether elasticity is present or not is best answered by working at very low velocities and pressures corresponding to the steep part of the curve where the deviations will be most easily detected.

So if we use a viscometer with small hydrostatic pressures and so arranged that one can work at different pressures, we have a very sensitive instrument to test whether POISEUILLE's law holds or not. Such a viscometer is the modification of the OSTWALD viscometer described by H. G. BUNGENBERG DE JONG (l.c.)<sup>1)</sup>. With such viscometers he investigated sols of agar, starch, iso-electric gelatin and acid gelatin, all at 40° C.

These all appeared to follow the law of POISEUILLE exactly. Miss VAN DER MADE<sup>2)</sup> investigated in the same way  $\text{CeO}_2$  sols, and

<sup>1)</sup> Rec. Trav. chim. **42**, 1 (1923). Further **43**, 35 and 189 (1924).

<sup>2)</sup> Diss. Utrecht 1922.

found very good agreement. LIER<sup>1)</sup> obtained the same result with acid and alkaline casein sols, TENDELOO<sup>2)</sup> with gum arabic and POSTMA<sup>3)</sup> with the sol of  $\text{SiO}_2$ . Since the fact that all these sols agree with POISEUILLE's law has been shown for the range of pressures where any deviation would be most easily detected, we can say with certainty that the sols mentioned would exhibit a viscosity uncomplicated by elasticity in other apparatuses under the same conditions and within the same limits of accuracy.

4. We come to the conclusion that sols consisting of only primary particles always follow POISEUILLE's law, but that deviations first appear when the primary particles have united to form greater aggregates either due to temperature gelation or due to slow or rapid electrolytic coagulation.

Fresh  $\text{V}_2\text{O}_5$ -sol follows POISEUILLE's law, but the investigations of FREUNDLICH and SCHALEK and of Wo. OSTWALD<sup>4)</sup> (which we have been able to confirm with the HESS apparatus at  $23^\circ$  and  $40^\circ$ ) show that old  $\text{V}_2\text{O}_5$  sols showed marked deviations. In these sols which show double refraction (as is also the case with sodium stearate) long needle shaped particles are present.

We are thus able to establish the fact that the deviations from POISEUILLE's law first appear after the formation of *complex* particles. Several theories may be put forward to explain this. DE JONG<sup>5)</sup> considers the reason to be that particles are broken up at greater rates of flow but coalesce again when the rate of flow becomes less. It may also be that the phenomenon depends on the particles not being spherical; this deviation being very slight in the case of the primary, but often very large for the secondary and higher particles. The  $\text{CeO}_2$  sol follows POISEUILLE's law even when the gelation has proceeded quite far, as Miss VAN DER MADE found. Since with this sol there was disagreement between her results and those of FREUNDLICH and SCHALEK (who found that  $\text{CeO}_2$  sol did not follow POISEUILLE's law in the HESS apparatus), we repeated this experiment with the result that we got good agreement also in the HESS apparatus as will be seen from the following table:

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<sup>1)</sup> Diss. Utrecht, 1924.

<sup>2)</sup> As yet unplublished.

<sup>3)</sup> Diss. Leiden, 1924.

<sup>4)</sup> Z. physik. Chem. **111**, 62 (1924).

<sup>5)</sup> Rec. Trav. Chim. **42**, 1 (1923).

Temperature	Pressures (mm. of Hg)	Ts/Tw
20°	60	1.56 <sup>6</sup>
	40	1.56 <sup>1</sup>
	20	1.56 <sup>2</sup>
	10	1.56 <sup>1</sup>

The fact that an ordinary sol with primary particles follows POISEUILLE's law is of great importance in the interpretation of viscosity measurements. In fact if this were not the case, simple relations like that of EINSTEIN would not be applicable for these systems<sup>1</sup>). The interpretation of viscosity measurements for lyophile sols would hence be very much more difficult.

The controversy over these phenomena became singularly subjective on account of the theoretical interpretations which the various workers attached to their results. Thus WO. OSTWALD<sup>2</sup>) has no hesitation in understanding by viscosity the combined effects of the internal friction of the liquid and the elasticity, since he is satisfied with the phenomenology of the matter. Whoever takes up the real standpoint of the physical chemist and tries to obtain a mechanical picture from the results of his viscosity measurements wishes to obtain from his measurements something capable of mechanical-kinetic interpretation.

Without for a moment wishing to minimise the importance of the elasticity phenomena, we, however, consider the uncomplicated viscosity a more repaying subject for physico-chemical research since it is more easily interpretable and will lead us sooner to a knowledge of the internal constitution of lyophilic systems.

*Utrecht, Oct. 1924.*

VAN 'T HOFF-*Laboratorium.*

<sup>1</sup>) Comp. KRUYT and DE JONG, Z. physik. Chem. **100**, 250 (1922).

<sup>2</sup>) Z. physik. Chem. **111**, 62 (1924).

**Astronomy.** — *"Report on the principal lines of research followed by me at the Union Observatory, Johannesburg, from 1923 November to 1924 October."* By EJNAR HERTZSPRUNG <sup>1)</sup>.

(Communicated at the meeting of November 29, 1924).

The practical astronomer is subject to many restrictions, which he will try to diminish as much as possible beforehand. The principal reasons for my stay at the Union Observatory, Johannesburg, are: firstly the excellent climate, and secondly our relatively limited knowledge of the Southern hemisphere. Additional attractions were the suitability of the Franklin Adams star camera to some of my researches, and the possibility of complete devotion to scientific research without being distracted by every day duties. I am greatly indebted to the director and staff of the Union Observatory for their readiness to help and effective assistance in many respects.

The Franklin Adams objective has an aperture of 254 mm and a focal length of 1123 mm, so that 1 mm on the plate equals 183".6. Plates 20 × 20 cm (the largest size for which Dr. SCHILT's microphotometer is adapted) thus represent an area of about 100 square degrees, and as the aperture nearly equals that of the „carte du ciel" refractors, half an hour's exposure will show stars of about the 14<sup>th</sup> photographic magnitude.

The scale of the plates being rather small, such faint stars will be closely packed in some regions of the Milky Way, but this circumstance will cause serious trouble in exceptional cases only.

Considering all possibilities the instrument seemed to be especially adapted to focal plates of faint variable stars. This being determined on, the question arose, whether it would be preferable to search for new variable stars in many different parts of the sky, or to investigate some selected regions only, taking a sufficiently large number of plates to determine the periods and light-curves for all the variable stars occurring on them. I have preferred the latter

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<sup>1)</sup> In 1923 an agreement was drawn up between the observatories at Johannesburg and Leiden, which has been approved by the respective governments, and according to which astronomers attached to either institute have the right to use the resources of the other (cf. Report of the director of the observatory at Leiden for the year 1923. *B. A. N.* II, 46, p. 31). As a result of this agreement Prof. HERTZSPRUNG left Leiden for Johannesburg on 1923 October 26.



course, the more so as in many cases the discovery of variable stars has not been followed up by a thorough investigation of the special stars. This abundancy of discoveries, which requires no special scientific training, is doubtlessly partly due to the sportive charm of this kind of work.

It may be expected, that the investigation of faint variable stars will give us many important clues about the structure of the galactic system. The more distant, and therefore *ceteris paribus* fainter, the star is, the more difficult it becomes to investigate its light spectroscopically, even only with respect to colour. Variability in brightness will remain within the range of our observational power for considerably fainter objects.

As regions of which a large number of plates will be taken, I have selected :

### 1. The great Magellanic cloud.

About one thousand variable stars in this cloud, which is completely covered by the  $20 \times 20$  cm plates, have been listed at Harvard Observatory, which still await final discussion. Though in some parts of the cloud the stars are so crowded, that the scale of the Franklin Adams plates is too small, a sufficient number of variable stars remains, which may safely be measured with the microphotometer.

Up till now 56 plates of this region have been taken, the exposure time being half an hour in the mean.

These plates have not yet been definitively measured, but it can now already be stated, that the greater part of the variable stars occurring in the great Magellanic cloud are of the  $\delta$  Cephei-type, a fact which has been noted previously at Harvard Observatory. No eclipsing variable stars have been found in this region up to the present time. On the contrary there are many variables of the RR Lyrae-type, but it is as yet uncertain whether these stars belong to the cloud, or are only accidentally projected on it.

### II. The region about $\eta$ Carinae.

This is one of the most interesting clouds of the Milky Way, and contains many relatively bright stars, whereas the faintest stars are not so abundant as to make the scale of the Franklin Adams plates too small for reliable measurement.

About a dozen Cepheid variables were already known in the region on a area of only 100 square degrees. I have added about double this number, principally by discovering many faint objects

of this type. This is important, as we must conclude that either the majority of these stars does not belong to a single cloud, or that the relation between period and luminosity, found by Miss LEAVITT for Cepheid variables in the small Magellanic cloud, does not hold in this region.

LUDENDORFF has pointed out, that the character of the light-curve of Cepheid variables depends systematically on the period. It is particularly striking that for periods of about 10 to 12 days the range of variation is small and the light-curve nearly symmetrical, whereas for shorter and longer periods the curves are very unsymmetrical. I have been able to confirm this remarkable result by means of several new Cepheids in the region about  $\gamma$  Carinae having periods of about 10 to 12 days. Any theory of the nature of Cepheid variation should take this fact into account.

Up to the present time very few eclipsing variables were known in this region. By means of the "Blinkmicroscope" I have added 44 new ones to their number, not counting some older variables, which were found to be of this type. The most remarkable fact with respect to this new group of eclipsing binaries is perhaps, that statistically they do not differ very much from those already known in the whole heavens, unless in apparent magnitude. The relative frequencies of the periods are similar. Another striking fact is, that the fraction of the period during which eclipse takes place, shows only small dispersion about a mean value of about  $1/10$ .

Of course stars with shorter duration of eclipse will more easily escape detection, but my impression is, that this circumstance is insufficient to explain the scarcity of eclipsing binaries of this kind. I am inclined to see in this fact a confirmation of the theory of fission, according to which the components of double stars, which have originated by fission, will not greatly increase their separation in the course of their further evolution. According to this hypothesis the period of an eclipsing variable will give an indication of the density at the moment of fission.

With increasing ability in the use of the Blinkmicroscope I have detected more and more variable stars with small range of variation. This is very welcome. As to the eclipsing binaries: two spherical stars of equal diameter and surface brightness cannot lose more than  $0^m.75$  in the combined magnitude by an eclipse. The sensitiveness of the common methods of discovery of variable stars being only about half a magnitude, it is evident, that a strong preference for the discovery of eclipsing binaries of large variation exists, e.g. systems consisting of a bright star of relatively small diameter and

a large relatively dark star. This observational selection of the material at our disposition up to the present time makes it difficult to use of for statistical applications.

Among the new eclipsing binaries found in the region near  $\eta$  Carinae one having the very short period of 0.3052 days and showing double eclipse deserves special mention (*B.A.N.* 56, 113). Only one case of this kind with still shorter period ( $d.237$ ) is known. Of another (*B.A.N.* 54 *d*) the range is unusually large, perhaps the largest known. Though no accurate determination of the range has as yet been made, I estimate it to be about  $4^m$ . Further it is worthy of mention, that the eclipsing binary *B.A.N.* 52 *d* shows an extraordinarily long phase of constant brightness during minimum, namely about  $\frac{1}{10}$  of the period, which is  $14^d.4$ . Such stars are of special interest, because it will be possible, as soon as our instruments have become sufficiently powerful, to determine the ratio of the masses of the components by measuring the change of the radial velocity of the fainter star during the total eclipse of the brighter.

In the latest catalogue of ephemerides of variable stars, published by the Bamberg Observatory (*V.J.S.* 58, 210; 1923) periods are given for 177 eclipsing binaries. These are distributed over 4 equal zones of the sky as follows

declination . . . . .	+ 90°	+ 30°	0°	— 30°	— 90°
number of eclipsing binaries	78	41	31	27	

It is evident from these numbers, how unequally the amount of work has been divided between the two hemispheres up till now. By the discovery of new variable stars in the region of  $\eta$  Carinae only I have added 36 to the last number for the most Southern zone.

The number of  $\delta$  Cephei-variables with known periods, taken over the whole sky, is about half that of the known eclipsing binaries. In the region of  $\eta$  Carinae I have found nearly the same proportion.

As the two plates which have been compared in the Blink microscope were always so selected, that the difference of the epoch amounted to a few days only, the variable stars found show nearly exclusively rapid variation. They belong with few exceptions to the eclipsing,  $\delta$  Cephei or RR Lyrae types. Of the last named type only a small number have been found. This is in good agreement with the fact that the known variable stars of this kind do not show galactic concentration, notwithstanding their low apparent brightness. This is important with respect to their large peculiar velocities. They may belong to the group of stars with large, with respect to the Galaxy possibly hyperbolic, velocities pointed out by Oort.

Further investigation of the distribution of variable stars of this type in different parts of the sky may be well worth while.

Among the few stars showing rapid variation, which do not belong to the three types mentioned above, one is of exceptional importance. This star (*B.A.N.* 52, 87) is faint or invisible on nearly all the plates. Only on the last three plates of five, which have been taken in succession on the same night, each with half an hour exposure time, the star is respectively about  $1^m.8$ ,  $1^m.1$  and  $0^m.75$  brighter than normal. This seems to be a Nova of exceptionally short duration. It may very well be, that Novae of this kind are not too scarce, notwithstanding the fact, that such phenomena have not been observed with certainty before. For it is evident, that they may easily escape detection. Only in the case that such a Nova of short duration is visible on several plates taken in the same night, there will be no doubt as to the reality of the phenomenon.

Up till now I have taken 408 plates of the region about  $\eta$  Carinae more or less fit for use, within a period of seven months. Attention has been paid to observe in different hour angles, in order to secure material fit for the determination of periods of variable stars. But there are cases, in which additional observations secured at observatories in different geographic longitudes will be desirable.

In addition to the two regions mentioned above I have begun to take series of plates of some other regions. But the time has not yet come to report on these more in detail.

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**Physics.** — “*On the Equation of State of Liquids and Solid Bodies at High and at Low Temperatures*”. By Dr. J. J. VAN LAAR.  
(Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of December 27, 1924).

## 1. Introduction.

Some five years ago <sup>1)</sup> I showed, that when in VAN DER WAALS' equation of state for liquids and gases, viz.

$$p + \frac{a}{v^2} = \frac{RT}{v-b}, \quad . . . . . (1)$$

$b$  is considered as a function of  $v$  (which VAN DER WAALS had already done in another way), and when the simple relation

$$b = \frac{b_g}{1 + \frac{b_g - b_0}{v}} \quad . . . . . (2)$$

is assumed for this, a perfect agreement — not only a qualitative, but also a quantitative one — is reached between the values for different quantities derived from the equation of state, and the experimental results; which so far had either not been the case, or in a much smaller degree. All this has been set forth more at length and more systematically in my book on the equation of state <sup>2)</sup>, to which I refer the interested reader. (Cf. in particular p. 74—79, 91 et seq., and further the Chapters II and III). I will only mention the following points here.

1. From (2) in connection with (1) follows the *almost-rectilinearity* of the locus  $\frac{1}{2}(D_1 + D_2) = f(T)$ , in which  $D_1$  and  $D_2$  represent resp. the densities of the coexisting liquid and gas phases.

2. The values derived e.g. for the coefficient of compressibility  $\beta_p$  now become more than three times greater than on assumption of

<sup>1)</sup> Compare inter alia my two papers in the *Recueil des Trav. Chim. des P. B.* **39**, 215—242 and 371—410 (1920).

<sup>2)</sup> “*Die Zustandsgleichung von Gasen und Flüssigkeiten, usw.*”, Leipzig L. Voss (1924). Compare also a paper published recently: “*Ueber die Flüssigkeitsdichten bei verschiedenen Temperaturen*” in the *Zeitschr. f. anorg. u. allg. Chemie* **140**, 52—60 (1924).

$b$  constant, in perfect harmony with the values found experimentally for this coefficient.

3. The *critical* quantities, e. g.  $r = v_k : b_k$ ,  $s = RT'_k : p_k v_k$ , the vapour-pressure coefficient  $f$ , are now in perfect agreement with the values found experimentally for them. Thus for ordinary substances  $r$  now becomes = 2,1 instead of 3,  $s$  becomes = 3,8 instead of 2 $\frac{1}{2}$ ,  $f$  becomes 7 instead of 4.

4. The coefficients of the general vapour-pressure equation  $\log p = -\frac{A}{T} - B \log T + C - DT$ , which may be calculated by means of the equation of state corrected by means of (2), agree again perfectly with the values found experimentally for them. Compare in the book cited particularly p. 296—304 (He, H<sub>2</sub>, Ar, C<sub>6</sub>H<sub>6</sub>), p. 287—296 (mercury and carbon), and p. 311—326 (the molten metals).

In this way I found in 1920 for *solid carbon* the theoretical vapour-pressure equation<sup>1)</sup>:

$$\log^{10} p_{\text{atm.}} = -\frac{47120}{T} + 9,4,$$

while in 1923 for the first time by an experimental way (method LANGMUIR) the equation

$$\log^{10} p_{\text{atm.}} = -\frac{47000}{T} + 9,3$$

was found by WERTENSTEIN and JEDRZEJEWSKI<sup>2)</sup>.

A better agreement with theoretical calculation — which according to the formulae derived by me was only based on the coefficient of expansion of graphite extrapolated to 4000°, in connection with the value of  $\sqrt{a}$  for carbon found from the additive fundamental values — could hardly be expected<sup>3)</sup>.

And this was also found for the other above-mentioned substances, and wherever in other cases the equation of state supplemented by (2) was applied.

Probably  $a$  and  $b_g$  are still functions of  $T$ ; I have, however, found that these two *temperature*-dependences always almost entirely neutralize each other, so that the simple assumption

<sup>1)</sup> Recueil 39, 647—655 (1920).

<sup>2)</sup> C.R. 177, 316—319 (1923).

<sup>3)</sup> Compare also Recueil 43, 598—599 (1924), C.R. 23 June 1924, p. 2250—2252. Further VAN LIEMPT, "Het toestandsdiagram van koolstof", Chem. Weekbl. 21, N<sup>o</sup>. 45 (1924), in particular the last two pages.

that *only*  $b$  is a function of the *volume* (for also the dependence of  $a$  on the volume may be neglected), which is rendered by (2), suffices in practice.

## 2. Significance of the found dependence on the volume of $b$ .

When (2) is substituted in (1), the equation:

$$p + \frac{a}{v^2} = \frac{RT}{v-b_0} \left( 1 + \frac{b_g - b_0}{v} \right), \quad \dots \quad (3)$$

is obtained after some reduction (Zustandsgl. p. 91). In this  $b_g$  represents the limiting value of  $b$  at  $v = \infty$ , and  $b_0$  that at  $v = v_0$ . If  $1,35m$  is assumed for  $b_0$  ( $m$  = real dimension of the molecule imagined spherical;  $1,35 = \frac{1}{2} \sqrt{2} : \frac{1}{6} \pi$  = coefficient in case of densest packing) and the theoretical value  $4m$  for  $b_g$ , then  $b_g$  becomes  $= 3b_0$ , so that it is also allowed to write:

$$p + \frac{a}{v^2} = \frac{RT}{v-b_0} \left( 1 + \frac{2b_0}{v} \right) \quad \dots \quad (3a)$$

The dependence of  $b$  on the volume represented by (2) is of course only an *apparent* one, ensuing from the necessity of applying a correction to the faulty equation of state  $p + \frac{a}{v^2} = \frac{RT}{v-b}$  with  $b$  constant. For instead of the Virial equation.

$$pv + \frac{a}{v} - RT \frac{b}{v-b} = RT,$$

which leads to  $p + \frac{a}{v^2} = \frac{RT}{v-b}$ , and in which  $RT \frac{b}{v-b}$  represents the so-called Virial of repulsion ( $b = 4m$ ), strictly speaking the equation

$$pv + \frac{a}{v} - RT \frac{b_g}{v-b_0} = RT \quad \dots \quad (3b)$$

ought to have been drawn up, which, with  $b_g = 4m = 3b_0$ , leads to the correct equation of state (3), which has been experimentally confirmed in every respect.

It is known that LORENTZ has found  $RT \frac{b_g}{v} = RT \frac{4m}{v}$  for the Virial of repulsion at  $v = \infty$ ; it now appears that when  $v$  is no longer  $= \infty$ , the expression  $RT \frac{b_g}{v-b_0}$  satisfies to the smallest volumes. In this  $b_g = 4m$  might be called the "*kinetic*" co-volume,  $b_0 = 1,35m$  the *true* co-volume.

It is remarkable, that when it is tried to derive the equation of state by an entirely different way (see § 4), viz. from certain thermodynamic relations in connection with the assumption that at higher temperatures also for liquids (and gases) the quantity  $\frac{3}{2} RT$  may be considered as the limiting value of the general expression for the kinetic energy, which has been derived quanta-theoretically e.g. by DEBYE — that *the same* expression (3<sup>a</sup>) is then obtained, though in this derivation there has been no question of any dependence of  $b$  on the volume.

Putting generally for liquids:

$$p + \frac{a}{v^2} = \lambda \frac{L}{v - c},$$

in which  $c$  is an arbitrary *constant*, and  $L$  represents the general expression for the progressive energy of the molecules, the following value is found in the way mentioned (see § 4):

$$\lambda = \frac{2}{3} \left( 1 + \frac{2c}{v} \right),$$

through which the equation of state for liquids (and gases) at higher temperatures ( $L = \frac{3}{2} RT$ ) immediately passes into (3<sup>a</sup>), when  $c = b_0$  is taken. It will appear in the following paragraph from a single example that this equation of state is in perfect agreement with the experimental data.

### 3. Experimental confirmation of (3) or (3<sup>a</sup>) for liquids at ordinary temperatures ( $T \sim \frac{1}{2} T_k$ ).

We will derive from (3) the value of the coefficient of compressibility  $\beta_p = -\frac{1}{v} \left( \frac{dv}{dp} \right)_t$ . Differentiation with respect to  $p$  ( $T$  constant) yields, when  $b_g - b_0 = \varphi$  is put in (3), from

$$p + \frac{a}{v^2} = \frac{RT}{v - b_0} \left( 1 + \frac{\varphi}{v} \right)$$

the equation:

$$1 - \frac{2a}{v^3} \left( \frac{dv}{dp} \right)_t = \left[ -\frac{RT}{(v - b_0)^2} \left( 1 + \frac{\varphi}{v} \right) - \frac{RT\varphi}{(v - b_0)v^2} \right] \left( \frac{dv}{dp} \right)_t,$$

from which follows:

$$\beta_p = -\frac{1}{v} \left( \frac{dv}{dp} \right)_t = 1 : \left[ -\frac{2a}{v^3} + \frac{RTv}{(v - b_0)^2} \left( 1 + \frac{\varphi}{v} \right) + \frac{RT\varphi}{(v - b_0)v} \right].$$

When according to the equation of state  $\frac{a}{v^2}$  is substituted in this



for  $\frac{RT}{v-b_0} \left(1 + \frac{\varphi}{v}\right)$ , in which, therefore, the external pressure is neglected, the following form results:

$$\frac{1}{\beta_p} = -\frac{2a}{v^3} + \frac{a}{v^2} \frac{v}{v-b_0} + \frac{a}{v^2} \frac{\varphi/v}{1 + \varphi/v} = \frac{a}{v^2} \frac{v}{v-b_0} - \frac{2a}{v^2} \frac{1 + \frac{1}{2} \varphi/v}{1 + \varphi/v}.$$

Now  $\frac{v}{v-b_0}$  is again  $= \frac{a/v}{RT} \left(1 + \frac{\varphi}{v}\right)$ ; hence finally:

$$\frac{1}{\beta_p} = \frac{a/v^2}{\frac{RT}{a/v} \left(1 + \frac{\varphi}{v}\right)} - 2 \frac{a}{v^2} \frac{1 + \frac{1}{2} \varphi/v}{1 + \varphi/v},$$

or

$$\beta_p = \frac{\frac{RT}{a/v} \left(1 + \frac{\varphi}{v}\right)}{\frac{a}{v^2} \left[1 - 2 \frac{RT}{a/v} \left(1 + \frac{1}{2} \frac{\varphi}{v}\right)\right]} = \frac{\frac{m}{f} \left(1 + \frac{\varphi}{v}\right)}{\frac{a}{v^2} \left[1 - 2 \frac{m}{f} \left(1 + \frac{1}{2} \frac{\varphi}{v}\right)\right]}, \quad \dots (4)$$

as  $a/v = fRT_k$  ( $f$  = vapour-pressure factor at  $T$ ) and  $m = T : T_k$ .

Since for ordinary substances  $f=7$  at  $m=1/2$ ,  $\frac{m}{f}$  becomes  $= \frac{1}{14}$ , hence approximately with  $\frac{\varphi}{v} = 2$ :

$$\beta_p = \frac{1/14}{a/v^2(1 - 1/14)} = \frac{0,3}{a/v^2}.$$

Without the factor  $1 + \varphi/v$  in (3), i. e. if  $b_0 = b_0$  had been put ( $b$  constant), the coefficient of compressibility would have therefore been at least  $1 + \varphi/v$  times, i. e. 3 times smaller. And now it actually appears from the following examples that values are found for  $\beta_p$ , which agree with (4); and not with the equation without  $1 + \varphi/v$ , hence with  $b$  constant, which equation would have had the simple

form  $\beta_p = \frac{m/f}{a/v^2(1 - 2m/f)}$ .

a. *Mercury*. (Cf. Zustandsgl. p. 114). Here  $m = T : T_k = = 295 : 1750 = 1 : 5,9$  at  $22^\circ \text{C}$ ., the value 4,1 being found for  $f$  from the vapour-tension at this temperature, so that  $m/f$  is  $= 1/24$ . We assume the value 3 for  $1 + \varphi/v = 1 + (b_g - b_0)/v = 1 + 2b_0/v$ , so that we obtain, when  $10^6 a = 17140$  is assumed at  $22^\circ$  for  $a$  (from vapour-pressure observations; cf. Zust.gl. p. 101) and  $10^6 v = 661$  (everything expressed in so-called "normal" units):

$$\beta_p = \frac{1/24 \times 3}{39250 (1 - 1/12 \cdot 2)} = \frac{1}{261700} = 3,82 \cdot 10^{-6} \text{ (per atm/cm}^2\text{)}.$$

The value found was  $3,9 \cdot 10^{-6}$  (per  $\text{kg}/\text{cm}^2$ ), so that the agreement may be considered good. (It follows really from BRIDGMAN's observations, that  $1 + \epsilon/v$  is somewhat greater than 3). But *without* the factor  $1 + \epsilon/v$  the value  $\frac{1/_{24}}{39250 (1 - 1/_{12})} = \frac{1}{863500} = 1,16 \cdot 10^{-6}$  would have been calculated, hence *3,3 times too small!*

*b. Ether.* (Zust.gl. p. 115). At  $20^\circ$   $\frac{5}{8} : 7 = \frac{1}{11}$  is found for  $m/f$ . ( $RT : a/v$  gives  $1,073 : (2413 \times 4618 \cdot 10^{-6})$ , as  $a/v_2$  is  $= 2413$  (loc. cit. p. 103), i. e.  $1 : 10,4$ . From BRIDGMAN's experiments I calculated  $8405 \cdot 10^6 : 4618 \cdot 10^6 = 1,82$  for  $\epsilon/v$ , so that  $1 + \epsilon/v$  becomes  $= 2,82$ . Hence we have:

$$\beta_p = \frac{1/_{10,4} \times 2,82}{2413 (1 - 1/_{1,1} \cdot 1,91)} = 178 \cdot 10^{-6},$$

while from 176 to 185 has been found (average 180), which is again in excellent harmony with the calculated value. The uncorrected value  $\frac{1/_{10,4}}{2413 (1 - 1/_{5,2})}$  would have been  $= 49 \cdot 10^{-6}$ , hence *3,6 times too small!*

*c. Ethylchloride* (Zust.gl. p. 115). We refer to the book cited, and will only mention that the calculated value of  $\beta_p$  is  $135 \cdot 10^{-6}$ , while AMAGAT likewise found  $135 \cdot 10^{-6}$ . The uncorrected value would have been  $34 \cdot 10^{-6}$ , i. e. *4 times too small!*

#### 4. Derivation of the equation of state from thermodynamic relations.

From the well-known thermodynamic formula

$$T \left( \frac{d^2 p}{dt^2} \right)_v = \left( \frac{dc_v}{dv} \right)_t \cdot \cdot \cdot \cdot \cdot \cdot \quad (5)$$

follows:

$$\left( \frac{dp}{dt} \right)_v = \int \frac{1}{T} \left( \frac{dc_v}{dv} \right)_t dt - \psi(v), \cdot \cdot \cdot \cdot \cdot \quad (a)$$

in which the meaning of  $\psi(v)$  will appear from what follows.

In order to be able to integrate the above equation quite generally at all temperatures, we apply the following expedient. According to DEBYE's well-known expression  $c_v$  is only a function of  $x_m = h\nu_m$ :  $kT = \theta$ ;  $T$ , in which the characteristic temperature  $\theta$  will, in general, still be a function of  $v$  and  $T$ . For according to the well-known expression

$$\theta = \frac{3.61}{\omega} 10^{-3} M^{1/2} D^{-1/2} \beta_p^{-1/2},$$

in which  $\omega$  is a numerical factor related to Poisson's coefficient  $\sigma$  (which is absent with liquids),  $\theta$  can be represented by

$$\theta = A v^{1/2} \beta_p^{-1/2} = A v^{2/3} \beta^{-1/2}$$

when the coefficient  $\beta = - \left( \frac{dv}{dp} \right)_i$  is introduced instead of  $\beta_p = - \frac{1}{v} \left( \frac{dv}{dp} \right)_i$ , which will prove to be more convenient. Hence

$$x_m = A v^{2/3} \beta^{-1/2} T^{-1}$$

is obtained for  $x_m = \theta : T$ .

From this follows, as  $\beta$  is still a function both of  $v$  and  $T$ :

$$\frac{1}{x_m} \left( \frac{dx_m}{dv} \right)_i = \frac{2}{3} \frac{1}{v} - \frac{1}{2} \frac{1}{\beta} \left( \frac{d\beta}{dv} \right)_i = - \frac{1}{v} \left[ - \frac{2}{3} + \frac{1}{2} \frac{v}{\beta} \left( \frac{d\beta}{dv} \right)_i \right];$$

$$\frac{1}{x_m} \left( \frac{dx_m}{dt} \right)_v = - \frac{1}{T} - \frac{1}{2} \frac{1}{\beta} \left( \frac{d\beta}{dt} \right)_v = - \frac{1}{T} \left[ 1 + \frac{1}{2} \frac{T}{\beta} \left( \frac{d\beta}{dt} \right)_v \right].$$

In consequence of this we get:

$$\left( \frac{dx_m}{dv} \right)_i = \frac{T}{v} \left( \frac{dx_m}{dt} \right)_v \times \frac{-2/3 + 1/2 \beta'_v}{1 + 1/2 \beta'_t} = \gamma \times \frac{T}{v} \left( \frac{dx_m}{dt} \right)_v,$$

in which  $\gamma$  is a numerical coefficient, which will in general still be a function of  $v$  and  $T$ ;  $\beta'_v$  being substituted for  $\frac{v}{\beta} \left( \frac{d\beta}{dv} \right)$  and  $\beta'_t$  for  $\frac{T}{\beta} \left( \frac{d\beta}{dt} \right)_v$  for brevity's sake.

The above equation (a) now passes into

$$\left( \frac{dp}{dt} \right)_v = \int \frac{1}{T} \left( \frac{dc_v}{dv} \right)_i = \int \frac{1}{T} \frac{dc_v}{dx_m} \left( \frac{dx_m}{dv} \right)_i = \int \frac{\gamma}{v} \frac{dc_v}{dx_m} \left( \frac{dx_m}{dt} \right)_v dt - \psi(v),$$

i. e.

$$\left( \frac{dp}{dt} \right)_v = \int \frac{\gamma}{v} \left( \frac{dc_v}{dt} \right)_v dt - \psi(v), \quad \dots \dots \dots (b)$$

through which — in consequence of the substitution of  $\left( \frac{dc_v}{dv} \right)_v$  by  $\left( \frac{dc_v}{dt} \right)_v$ , which has been effected by the aid of  $x_m$  and the introduced coefficient  $\gamma$  — the integration with respect to  $T$  has been rendered possible; since the dependence of  $\gamma$  on the temperature will pract-

ically entirely disappear from the result, as will be shown in § 5. The integration of (b) gives:

$$\left(\frac{dp}{dt}\right)_v = \frac{\gamma_1}{v} c_v - \psi(v), \quad . . . . . (c)$$

which, once more integrated with respect to  $T$  ( $c_v$  being  $= \left(\frac{dE_t}{dt}\right)_v$ ), leads to

$$p + f(v) = \frac{\gamma_2}{v} E_t - T \psi(v), \quad . . . . . (d)$$

in which according to § 5  $\gamma_1$  and  $\gamma_2$  will differ only exceedingly little from the limiting value at  $T = \infty$  of the coefficient  $\gamma$  above introduced, viz. from

$$\gamma = \frac{-\frac{1}{2} + \frac{1}{2} \beta'_v}{1 + \frac{1}{2} \beta'_t}, \quad . . . . . (6)$$

which limiting value will appear to contain the factor  $\frac{v}{v-b_0}$  for liquids.

The integration constant  $f(v)$  remains thermodynamically undetermined, and can be determined only by considerations of a kinetic nature. (is  $= a/v^2$  for liquids).

With regard to  $T\psi(v)$  it may be stated that this is evidently  $= \frac{\gamma_1}{v} (\mu - \frac{1}{2}) RT$ , as in the equation for  $p$  according to the usual kinetic derivation (e.g. by means of the Virial theorem) *not* the whole energy will occur in the second member, but only the *progressive* part of the energy of the molecules ( $L$ ) — i.e. with exclusion of the potential energy of the forces acting between the atoms in the molecule. Hence  $(\mu - \frac{1}{2}) RT$ , which relates to the said potential energy, must be subtracted from  $E_t$ . For mon-atomic substances  $\mu$  is therefore  $= \frac{1}{2}$ , for di-atomic substances  $= \frac{1}{2}$ , etc. Hence we may write instead of (d):

$$p + f(v) = \frac{\gamma_2}{v} L \quad . . . . . (7)$$

The considerations given in this paragraph are namely not only valid for solid substances, but also for liquids and gases; when it is only assumed, that the value of  $L$  then depends on  $x_m = \theta : T$  (according to the relation of DEBYE) in quite the same way as for solid bodies. But according to the formula holding for  $\theta$  this quantity has then



a much smaller value than for solid bodies. That the degeneration of the progressive energy  $L$  may be assumed to take place in an entirely analogous way in liquids and in gases as in solid bodies, has, indeed, already been assumed by many physicists (among others by KEESOM in many of his papers).

### 5. Determination of $\gamma_2$ (or $\lambda$ ) for liquids and gases.

We shall now proceed to the determination of the value of  $\gamma_2$ , or rather — starting from the known form of the equation of state for liquids and gases, viz.

$$p + \frac{a}{v^2} = \frac{\lambda}{v-b_0} L, \quad \dots \quad (8)$$

of the value of the quantity  $\lambda = \gamma_2 \frac{v-b_0}{v}$ , in which  $\lambda$  will be in the neighbourhood of 2, and in which the quantity  $v:(v-b_0)$  will no longer occur directly as a factor.

At not too low temperatures the expansion into series

$$L = \frac{3}{2} RT \left( 1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} + \frac{1}{90720} \frac{\theta^6}{T^6} - \text{etc.} \right) \quad (a)$$

holds for  $L$ , at least when the zero-point energy is also taken into account in the expression

$$L = \frac{1}{2} \frac{RT}{x_m} \int_0^{x_m} \left( \frac{1}{2} + \frac{1}{e^x - 1} \right) x^2 dx.$$

( $\frac{1}{2} x^2 dx$  under the integral sign). For otherwise  $L$  would become  $= \frac{3}{2} RT \left( 1 - \frac{3}{8} \frac{\theta}{T} + \frac{1}{20} \frac{\theta^2}{T^2} - \text{etc.} \right)$ , which would not approach to  $\frac{1}{2} RT$  even at the highest temperatures, but which would always remain the *finite* value of  $\frac{1}{16} R\theta$  distant from it.

The quantity  $\theta$  can be represented as function of  $T$  by

$$\theta = \theta_0 \left( 1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right),$$

in which  $\theta_0$ ,  $\varphi_1$ ,  $\varphi_2$ , etc. are still functions of  $v$ . For in  $\theta^2 = A^2 v^{4/3} \beta^{-1}$  (see § 4)  $\beta^{-1}$  will have the form  $a + bT + \frac{c}{T} + \dots$  (see § 6). With regard to  $\lambda$  we may write:

$$\lambda = \lambda_0 \left( 1 + \frac{\alpha}{T^2} + \dots \right),$$

in which terms with  $1/T$  and  $1/T^2$  must be omitted, as it will at once appear, that when the expansion into series of  $L$  is not pursued further than  $\theta^2/T^2$ , the expansion into series of  $\lambda$  must be continued to  $\alpha/T^2$ . But since only two equations will then be obtained for the two unknown quantities  $\lambda_0$  and one coefficient, there can occur only one coefficient in the expansion into series of  $\lambda$ . If the expansion of  $L$  is carried up to  $\theta^2/T^2$ , that of  $\lambda$  must go to  $\alpha'/T^2$ , and there will be one equation more for the determination of the new coefficient  $\alpha'$ . Etc. It is, therefore, clear that in the expansion into series of  $\lambda$  the terms with  $1/T$  and  $1/T^2$  will be absent.

Like  $\lambda$ , the coefficient  $\alpha$  is again a function of  $v$ .

Finally, as will appear in § 6, the quantity  $\gamma$  in (6) will be represented by

$$\gamma = \gamma_0 \frac{1 + \delta_1 T}{1 + \delta_2 T},$$

in which further terms with  $1/T$  may be omitted, and in which  $\gamma_0$ ,  $\delta_1$ , and  $\delta_2$  will still be functions of  $v$ .

We may now write:

$$\frac{\theta^2}{T^2} = \theta_0^2 \left( \frac{\varphi_1}{T} + \frac{1}{T^2} + \frac{\varphi_2}{T^3} \right); \frac{\theta^4}{T^4} = \theta_0^4 \left( \frac{\varphi_1^2}{T^2} + \frac{2\varphi_1}{T^3} \right); \frac{\theta^6}{T^6} = \theta_0^6 \frac{\varphi_1^3}{T^3},$$

when in what follows one restricts oneself to terms with  $1/T^2$ . This lowering of the degree with respect to  $T$  has of course been brought about by the term with  $T$  in the above expression for  $\theta^2$ . Hence we have according to (a):

$$L = \frac{3}{2} R \left[ T + \frac{1}{20} \theta_0^2 \left( \varphi_1 + \frac{1}{T} + \frac{\varphi_2}{T^2} \right) - \frac{1}{1680} \theta_0^4 \left( \frac{\varphi_1^2}{T} + \frac{2\varphi_1}{T^2} \right) + \frac{1}{90720} \theta_0^6 \left( \frac{\varphi_1^3}{T^2} \right) \right] = \frac{3}{2} R \cdot Q,$$

and from this:

$$\begin{aligned} c_v &= \left( \frac{dE_t}{dt} \right)_v = \left( \frac{d(L + (\mu - \frac{3}{2}) RT)}{dt} \right)_v \quad (\text{cf. § 4}) = \\ &= \frac{3}{2} R \left[ 1 + \frac{1}{20} \theta_0^2 \left( -\frac{1}{T^2} - \frac{2\varphi_2}{T^3} \right) - \frac{1}{1680} \theta_0^4 \left( -\frac{\varphi_1^2}{T^2} - \frac{4\varphi_1}{T^3} \right) + \right. \\ &\quad \left. + \frac{1}{90720} \theta_0^6 \left( -\frac{2\varphi_1^2}{T^3} \right) \right] + \left( \mu - \frac{3}{2} \right) R, \end{aligned}$$

hence:

$$\begin{aligned} \left( \frac{dc_v}{dt} \right)_v &= \frac{3}{2} R \left[ \frac{1}{20} \theta_0^2 \left( \frac{2}{T^3} + \frac{6\varphi_2}{T^4} \right) - \frac{1}{1680} \theta_0^4 \left( \frac{2\varphi_1^2}{T^3} + \frac{12\varphi_1}{T^4} \right) + \right. \\ &\quad \left. + \frac{1}{90720} \theta_0^6 \left( \frac{6\varphi_1^2}{T^4} \right) \right]. \end{aligned}$$

With  $\lambda = \lambda_0 \left(1 + \frac{\alpha}{T^3}\right)$  we get:

$$\lambda L = \lambda_0 \cdot \frac{3}{2} R \left( Q + \frac{\alpha Q}{T^3} \right) = \lambda_0 \cdot \frac{3}{2} R \left( Q + \frac{\alpha(T + \dots)}{T^3} \right),$$

from which it appears that the expansion into series for  $\lambda$  need not go further than  $\alpha/T^3$ , when  $Q$  is not continued further than  $1/T^3$  (see above). From the equation of state (8) follows, as  $\frac{d^2}{dt^2} \left( \frac{3}{2} R Q \right)_v = \left( \frac{d^2 L}{dt^2} \right)_v = \left( \frac{dc_v}{dt} \right)_v$ , according to the above:

$$\left( \frac{d^2 p}{dt^2} \right)_v = \frac{\lambda_0}{v - b_0} \left[ \left( \frac{dc_v}{dt} \right)_v + \frac{3}{2} R \frac{6\alpha}{T^4} \right].$$

Now according to the thermodynamic relation (5), in connection with our transformation of  $\left( \frac{dc_v}{dv} \right)_t$  into  $\left( \frac{dc_v}{dt} \right)_v$  by means of  $\gamma$ , which we developed in § 4, the following equation ensues:

$$\left( \frac{d^2 p}{dt^2} \right)_v = \frac{1}{T} \left( \frac{dc_v}{dv} \right)_t = \frac{\gamma}{v} \left( \frac{dc_v}{dt} \right)_v,$$

so that

$$\frac{\lambda_0}{v - b_0} \left[ \left( \frac{dc_v}{dt} \right)_v + \frac{3}{2} R \frac{6\alpha}{T^4} \right] = \frac{\gamma}{v} \left( \frac{dc_v}{dt} \right)_v = \frac{\gamma_0}{v} \frac{1 + \delta_1 T}{1 + \delta_2 T} \left( \frac{dc_v}{dt} \right)_v.$$

According to the above, the following form may be written for  $\left( \frac{dc_v}{dt} \right)_v$ :

$$\begin{aligned} \left( \frac{dc_v}{dt} \right)_v = \frac{3}{2} R \left[ \frac{1}{T^3} \left( \frac{1}{10} \theta_0^2 - \frac{1}{840} \theta_0^4 \varphi_1^2 \right) + \right. \\ \left. + \frac{1}{T^4} \left( \frac{3}{10} \theta_0^2 \varphi_2 - \frac{1}{140} \theta_0^4 \varphi_1 + \frac{1}{15120} \theta_0^6 \varphi_1^3 \right) \right], \end{aligned}$$

or also

$$\left( \frac{dc_v}{dt} \right)_v = \frac{3}{2} R \left( \frac{A}{T^3} + \frac{B}{T^4} \right).$$

Hence, when both members of the above equation are divided by  $\frac{3}{2} R$ , and multiplied by  $1 + \delta_2 T$ , the following equation is obtained:

$$\lambda_0 \frac{v}{v - b_0} (1 + \delta_2 T) \left[ \frac{A}{T^3} + \frac{B + 6\alpha}{T^4} \right] = \gamma_0 (1 + \delta_1 T) \left( \frac{A}{T^3} + \frac{B}{T^4} \right),$$





is required (see § 4). With regard to  $\beta$  it may be stated that from (8), viz.

$$p + \frac{a}{v^2} = \frac{\lambda L}{v - b_0} = \lambda_0 \frac{^{1/2} RT}{v - b_0} \left( 1 + \frac{1}{20} \frac{\theta^2}{T^2} - \dots \right),$$

with neglect of  $a/T^2$  in  $\lambda = \lambda_0 (1 + a/T^2)$ , and even of the term  $\theta^2/T^2$ , as having no influence on the result, follows:

$$1 - \frac{2a}{v^3} \left( \frac{dv}{dp} \right)_t = -\lambda_0 \frac{^{1/2} RT}{(v - b_0)^2} \left( \frac{dv}{dp} \right)_t,$$

from which

$$\beta = - \left( \frac{dv}{dp} \right) = 1 : \left[ -\frac{2a}{v^3} + \lambda_0 \frac{^{1/2} RT}{(v - b_0)^2} \right] = 1 : N.$$

When determining  $\beta'_v = \frac{v}{\beta} \left( \frac{d\beta}{dv} \right)_t$  and  $\beta'_t = \frac{T}{\beta} \left( \frac{d\beta}{dT} \right)_v$  from this, a grave error would be committed, if e. g.  $\lambda_0 \frac{^{1/2} RT}{v - b_0}$  was substituted for  $a/v^2$  according to the equation of state, with neglect of  $p$ . For though  $p$  may safely be neglected with regard to  $a/v^2$ , this is *not* the case with  $\left( \frac{dp}{dv} \right)_t = -\frac{1}{\beta}$ , which quantity runs into thousands (and for solid bodies into millions). For  $\beta$  must be differentiated with respect to  $v$  with  $T$  constant. In the same way the dependence on the temperature of  $\beta$ ,  $v$  constant, would be estimated quite wrongly, when the substitution mentioned was executed. For  $\left( \frac{dp}{dT} \right)_v$  is likewise very great. Such substitutions may only be made *after* the necessary differentiations described have been carried out (in which certain quantities must remain constant). A most elementary truth, but which is frequently overlooked!

We now get:

$$\beta'_v = \frac{v}{\beta} \left( \frac{d\beta}{dv} \right)_t = -\frac{v}{N} \left( \frac{dN}{dv} \right)_t = \frac{-\frac{6a}{v^3} + 2\lambda_0 \frac{^{1/2} RT v}{(v - b_0)^2}}{-\frac{2a}{v^3} + \lambda_0 \frac{^{1/2} RT}{(v - b_0)^2}},$$

and for  $\beta'_t$ :

$$\beta'_t = \frac{T}{\beta} \left( \frac{d\beta}{dT} \right)_v = -\frac{T}{N} \left( \frac{dN}{dT} \right)_v = \frac{-\lambda_0 \frac{^{1/2} RT}{(v - b_0)^2}}{-\frac{2a}{v^3} + \lambda_0 \frac{^{1/2} RT}{(v - b_0)^2}}.$$

This yields according to (6):

$$\gamma = \frac{-\frac{2}{3} \left( -\frac{2a}{v^2} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right) + \frac{1}{2} \left( -\frac{6a}{v^2} + 2\lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right)}{\left( -\frac{2a}{v^2} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right) + \frac{1}{2} \left( -\lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right)},$$

or

$$\begin{aligned} \gamma &= \frac{-\frac{5}{3} \frac{a}{v^2} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \left( \frac{v}{v-b_0} - \frac{2}{3} \right)}{-\frac{2a}{v^2} + \frac{1}{2} \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2}} = \\ &= \frac{5}{6} \frac{1 - \frac{1}{5} \lambda_0 \frac{^{3/2}RT}{a/v} \frac{v^2}{(v-b_0)^2} \frac{v+2b_0}{v-b_0}}{1 - \frac{1}{4} \lambda_0 \frac{^{3/2}RT}{a/v} \frac{v^2}{(v-b_0)^2}}. \end{aligned}$$

Also in this case we have not replaced  $a/v^2$  by its value from the equation of state with neglect of  $p$ , because in formula (9) derived above the quantities  $\delta_1$  and  $\delta_2$  in  $\gamma = \gamma_0 \frac{1 + \delta_1 T}{1 + \delta_2 T}$  are the *pure* coefficients of  $T$ , calculated from an equation, in which only  $v$  and  $T$  occur.

Now the formula (9) mentioned yields immediately:

$$\lambda_0 = \frac{v-b_0}{v} \gamma_0 \frac{\delta_1}{\delta_2} = \frac{v-b_0}{v} \cdot \frac{5}{6} \left( \frac{4}{5} \cdot \frac{v+2b_0}{v-b_0} \right) = \frac{2}{3} \left( 1 + \frac{2b_0}{v} \right), \quad (11)$$

so that (8), with neglect of  $a/T^2$  in  $\lambda_0 (1 + a/T^2)$ , passes into

$$p + \frac{a}{v^2} = \frac{^{3/2}L}{v-b_0} \left( 1 + \frac{2b_0}{v} \right), \quad \dots \dots \dots (12)$$

i. e. our equation (3<sup>a</sup>) in § 2, as at higher temperatures  $L = ^{3/2}RT$ . Hence — making use of the thermodynamic relation (5) and of the general expression for  $E_t$  or  $L$  (DEBYE) at higher temperatures, where the expansion into series (a) of § 5 is valid — a value, which is *in perfect agreement* with the coefficient found by us in § 2 by an entirely different way, has been found for the coefficient  $\lambda$ , which had remained quite undetermined in (8). We may point out that (12) might also have been written in the form

$$p + \frac{a}{v^2} - RT \frac{3b_0}{v(v-b_0)} = \frac{RT}{v},$$

in which  $RT \frac{3b_0}{v-b_0}$  may be interpreted as repulsive Virial (cf. § 2).

Accordingly at *higher* temperatures the equation of state

$$v + \frac{a}{v^2} = \frac{2/3 L}{v - b_0} \left( 1 + 2 \frac{b_0}{v} \right) = \frac{RT \left( 1 + \frac{1}{20} \frac{\theta^2}{T^2} - \dots \right)}{v - b_0} \left( 1 + 2 \frac{b_0}{v} \right)$$

holds for *liquids* (and *gases*); which approaches to

$$p + \frac{a}{v^2} = \frac{RT}{v - b_0} \left( 1 + 2 \frac{b_0}{v} \right) = \frac{3 RT}{v - b_0} \left( 1 - \frac{2}{3} \frac{v - b_0}{v} \right)$$

at sufficiently high temperature. As we have seen, this equation of state with the factor  $1 + 2 \frac{b_0}{v}$  at  $RT$  is in harmony with the experimental data concerning the straight diameter, coefficient of compressibility, critical quantities, vapour-pressure equation, etc. It immediately ensues from the dependence on the volume of  $b$  in  $p + \frac{a}{v^2} = RT : (v - b)$  found by us, but also from the thermodynamic formula  $T \left( \frac{d^2 p}{dv^2} \right)_v = \left( \frac{dc_n}{dv} \right)_t$  in connection with DEBYE's quanta-theoretical expansion into series for  $L$ .

For gases we have  $v = \infty$ , and  $\lambda$  becomes  $= \lambda_0 = \frac{2}{3}$ , so that simply  $p = RT : v$ .

At *very low* temperature in the neighbourhood of  $T = 0$  we must use another expansion into series for  $L$ . The further development of this case will be treated in the sequel to this paper, in which also the equation of state will be derived for *solid* substances both at high and at low temperatures.

### 7: Concluding remark. (A thermo-dynamic sophism).

According to (c) of § 4  $\left( \frac{dp}{dt} \right)_v$  will be  $= \frac{\gamma_1}{v} c_v$ , when  $\psi(v) = 0$  may be put, i. e. when  $\left( \frac{dp}{dt} \right)_v$  at  $T = 0$  converges to zero, parallel to  $c_v$ . But then the coefficient of expansion will also converge to 0 parallel to  $c_v$ . For from the known relation

$$\left( \frac{dv}{dt} \right)_p = - \left( \frac{dv}{dp} \right)_t \times \left( \frac{dp}{dt} \right)_v \quad \text{or} \quad \alpha_t = \beta_p \times s, \dots \quad (13)$$

in which  $\alpha_t = \frac{1}{v} \left( \frac{dv}{dt} \right)_p$  is the coefficient of expansion,  $\beta_p = \frac{1}{v} \left( \frac{dv}{dp} \right)_t$  the coefficient of compressibility, and  $\left( \frac{dp}{dt} \right)_v$  the coefficient of tension, then follows immediately:

$$\alpha_t = \beta_p \times \frac{\gamma_1}{v} c_v, \quad . . . . . (13a)$$

in which  $\beta_p$  will remain finite down to the lowest temperature, and  $\gamma_1$  is a numerical coefficient, so that  $\alpha_t$  will approach 0 proportional to  $c_v$ .

This property is, however, proved by some<sup>1)</sup> quasi-thermodynamically in the following wonderful way.

It is known that the general equation

$$dQ = c_p dt + l_p dp$$

leads to the equation

$$dS = \frac{c_p}{T} dt + \frac{l_p}{T} dp$$

for the entropy, when  $T$  and  $p$  are chosen as independent variables, in which  $l_p = \left(\frac{dQ}{dp}\right)_t = -T \left(\frac{dv}{dt}\right)_p$ , just as the quantity  $l_v$  is  $= T \left(\frac{dp}{dt}\right)_v$  in  $dQ = c_v dt + l_v dv$ . In consequence of this we have:

$$dS = \frac{c_p}{T} dt - \left(\frac{dv}{dt}\right)_p dp,$$

hence, according to well-known rules of integration, in which e.g.  $T$  must be kept constant in the second integral, and equal to the lowest limit of the first integral:

$$S = \int_0^T \frac{c_p}{T} dt - \int_0^p \left(\frac{dv}{dt}\right)_p dp, \quad . . . . . (a)$$

because  $S_0$  disappears in  $S = S_0$  at  $T = 0$ ,  $p = 0$  ( $v = v_0$ ).

This expression is sometimes shortened into

$$S = \int_0^T \frac{c_p}{T} dt, \quad . . . . . (b)$$

which is correct, when the coefficient of expansion  $\left(\frac{dv}{dt}\right)_p$  is assumed to approach 0 with  $c_v$  at  $T = 0$  (see above). But now the shortened formula thus obtained is used to prove, that e.g.  $\left(\frac{dv}{dt}\right)_p$  approaches 0 at  $T = 0$ !!

This marvellous reasoning runs as follows. From (cf. (b))

<sup>1)</sup> Cf. inter alia PLANCK, Thermodynamik (1921), p. 276.



$$\left(\frac{dS}{dp}\right)_t = \int_0^T \frac{1}{T} \left(\frac{dc_p}{dp}\right)_t dt = \int_0^T - \left(\frac{d^2v}{dt^2}\right)_p dt = - \left(\frac{dv}{dt}\right)_p + \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)}$$

follows immediately,  $\left(\frac{dS}{dp}\right)_t$  being  $= - \left(\frac{dv}{dt}\right)_p$ , that  $\left(\frac{dv}{dt}\right)_p$  must necessarily be  $= 0$  at  $T=0$  (PLANCK, loc. cit.)!!

In reality *nothing* has been proved; for the formula, on which the reasoning is based, is only correct if it is assumed *beforehand*, that the thesis that is to be proved, *has already been proved*.

When, however, the second integral in (a) is *not* neglected, the following equation ensues:

$$\left(\frac{dS}{dp}\right)_t = \left[ - \left(\frac{dv}{dt}\right)_p + \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)} \right] - \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)}$$

hence

$$\left(\frac{dS}{dp}\right)_t = - \left(\frac{dv}{dt}\right)_p$$

a known thermodynamic formula, which of course might much quicker be written down directly from the original equation

$$dS = \frac{c_p}{T} dt - \left(\frac{dv}{dt}\right)_p dp!$$

The *valid* proof, that  $\left(\frac{dv}{dt}\right)_p$  really approaches to 0 parallel to  $c_v$  for solid substances, can only be furnished when it is *assumed* (see above), or proved in an independent way, that  $\psi(v) = 0$  in (c) of § 4, in other words that  $\left(\frac{dp}{dt}\right)_v$  converges to 0 at  $T = 0$ . And inversely,

when the approach of  $\left(\frac{dv}{dt}\right)_p$  is assumed to be known, the approach of  $\left(\frac{dp}{dt}\right)_v$  to 0 can be derived from (13), from which it then *follows*, that  $\psi(v)$  must be  $= 0$ .

But "proofs" like the above, which are no proofs at all, should be guarded against. Unfortunately in many books from a certain school, recently published on these subjects, various new, often very questionable curtailed "thermodynamic" formulae are found; of which the elder generation never dreamt, and which — the above proves it — should be treated with the greatest caution.

*Tavel sur Clarens, Suisse,*

December 1924.

**Mathematics.** — “*On the index of summability*”. By M. J. BELINFANTE. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of October 25, 1924).

In a previous article <sup>1)</sup> the question was raised whether a series which is joinable of order  $p + 1$  (i. e. finite  $(C, p)$  and summable  $(C, p + 1)$ ) could possess an index  $> p$ . After unsuccessful trials to construct such a series I succeeded in proving that the index of a series which is summable of order  $p + 1$  must be  $\leq p$  (§ 1). The converse however is not true as may be seen from an example in our previous article <sup>2)</sup>.

The chief interest of the joinability of a series lies in the theorem that the product of a series which is joinable of order  $p$  by a series which is summable of order  $q$ , is summable of order  $p + q$  <sup>3)</sup>. Now, if it were allowed to substitute the words “which has an index  $\leq p - 1$ ” instead of the words “which is joinable of order  $p$ ”, then the notion of summability would be of little importance, as the former theorem about the multiplication would be an immediate consequence of the modified theorem and the theorem of § 1. By an example we will prove in § 2 that the modified theorem is not true: hence it may happen that the original theorem about the multiplication gives more result than that of CHAPMAN, as has been observed on a former occasion. <sup>4)</sup>

### § 1.

We consider the series  $\Sigma a_n = a_1 + a_2 + \dots$  and its derivate  $\Sigma b_n = b_1 + b_2 + \dots$  where  $b_n = n a_n$ . We denote the mean values of order  $p$  of  $\Sigma a_n$  by  $\frac{S_n^{(p+1)}}{A_n^{(p+1)}}$ , those of  $\Sigma b_n$  by  $\frac{T_n^{(p+1)}}{A_n^{(p+1)}}$ . Now we have the following relation: <sup>5)</sup>

<sup>1)</sup> “On Generalisations of the Notion of Absolute Convergence”. These Proceedings, Vol. XXVII p. 686.

<sup>2)</sup> L.c., p. 690.

<sup>3)</sup> “A Generalisation of MERTENS theorem.” These Proceedings, Vol. XXVI, p. 203.

<sup>4)</sup> These Proceedings, Vol. XXVI, p. 211.

<sup>5)</sup> For the notation, see these Proceedings, Vol. XXVII, p. 34.

$$\frac{T_n^{(p)}}{A_n^{(\nu)}} = (n+p) \frac{S_n^{(p)}}{A_n^{(\nu)}} - (n+p-1) \frac{S_n^{(p+1)}}{A_n^{(\nu+1)}} \dots \dots \dots (1)$$

Indeed:

$$\begin{aligned} T_n^{(p)} &= A_n^{(p)} b_1 + \dots + A_1^{(p)} b_n = A_n^{(p)} a_1 + \dots + A_1^{(p)} n a_n = \\ &= n \{ A_n^{(p)} a_1 + \dots + A_1^{(p)} a_n \} - \{ A_n^{(p)} (n-1) a_1 + \dots + A_2^{(p)} a_{n-1} \}. \end{aligned}$$

Substituting

$$(n-1) A_n^{(p)} = p A_n^{(p+1)} - p A_n^{(p)} \text{ and } S_n^{(p)} = A_n^{(p)} a_1 + \dots + A_1^{(p)} a_n$$

we become

$$\begin{aligned} T_n^{(p)} &= n S_n^{(p)} - p \{ A_n^{(p+1)} a_1 + \dots + A_1^{(\nu+1)} a_n \} + p \{ A_n^{(p)} a_1 + \dots + A_1^{(\nu)} a_n \} = \\ &= n S_n^{(p)} - p S_n^{(p+1)} + p S_n^{(p)}. \end{aligned}$$

Since  $A_n^{(p)} = \frac{p}{n+p-1} \cdot A_n^{(p+1)}$  we have

$$\frac{T_n^{(p)}}{A_n^{(\nu)}} = (n+p) \frac{S_n^{(p)}}{A_n^{(\nu)}} - (n+p-1) \frac{S_n^{(p+1)}}{A_n^{(\nu+1)}}.$$

We need the following lemma:

Whatever be  $x > 0$  it is possible to find two positive numbers  $k_1(x)$  and  $k_2(x)$  so that

$$k_1(x) < \frac{A_n^{(x)}}{n^x - 1} < k_2(x) \dots \dots \dots (2)$$

for every  $n$ .

This is a known result which may be easily deduced from the relations:

$$\begin{aligned} \frac{d}{dx} \cdot \log \frac{A_n^{(x)}}{n^{x-1}} &= \frac{1}{x} + \frac{1}{x+1} + \dots + \frac{1}{x+n-2} - \log n \\ \log \frac{x+n-1}{x} &< \frac{1}{x} + \frac{1}{x+1} + \dots + \frac{1}{x+n-2} < \log \frac{x+n-1}{x} + \frac{1}{x} \end{aligned}$$

by integrating between  $x$  and 1.

We now prove the following result:

**Theorem.** If  $\Sigma a_n$  is joinable of order  $p$  (i.e. summable  $(C, p)$  and finite  $(C, p-1)$ ), then the index of  $\Sigma a_n$  cannot exceed  $p-1$ .

**Proof.** We have to prove that for  $i > 0$   $\frac{S_n^{(p+i)}}{A_n^{(\nu+i)}}$  tends to a limit

as  $n \rightarrow \infty$ . Since by hypothesis  $\frac{S_n^{(\nu+1)}}{A_n^{(\nu+1)}} \rightarrow s$  we have also  $\frac{S_n^{(p+i+1)}}{A_n^{(p+i+1)}} \rightarrow s$  and hence by formula (1):

$$\lim_{n \rightarrow \infty} \left\{ \frac{S_n^{(\nu+i)}}{A_n^{(\nu+i)}} - \frac{1}{n+p+i} \cdot \frac{T_n^{(\nu+i)}}{A_n^{(\nu+i)}} \right\} = \lim_{n \rightarrow \infty} \frac{n+p-1+i}{n+p+i} \cdot \frac{S_n^{(p+i+1)}}{A_n^{(p+i+1)}} = s.$$

Hence it is sufficient to prove:  $\frac{1}{n} \cdot \frac{T_n^{(\nu+i)}}{A_n^{(\nu+i)}} \rightarrow 0$ .

Now we have whatever be  $k$  between 1 and  $n$ :

$$\begin{aligned} T_n^{(\nu+i)} &= \{A_1^{(i)} T_n^{(\nu)} + \dots + A_k^{(i)} T_{n-k+1}^{(\nu)}\} + \{A_{k+1}^{(i)} T_{n-k}^{(\nu)} + \dots + A_n^{(i)} T_1^{(\nu)}\} \\ &= I + II. \end{aligned}$$

By hypothesis we have  $\left| \frac{S_n^{(p)}}{A_n^{(\nu)}} \right| < K$  and hence with the aid of formula (1):

$$\frac{1}{n} \left| \frac{T_n^{(\nu)}}{A_n^{(\nu)}} \right| = \frac{1}{n} \left| (n+p) \frac{S_n^{(p)}}{A_n^{(\nu)}} - (n+p-1) \frac{S_n^{(\nu+1)}}{A_n^{(\nu+1)}} \right| < C.$$

Substituting this we get:

$$|I| < C \{A_1^{(i)} \cdot n A_n^{(\nu)} + \dots + A_k^{(i)} \cdot (n-k+1) A_{n-k+1}^{(\nu)}\}$$

We have  $A_r^{(\nu)} \geq A_{r+1}^{(\nu)}$ , if  $p \leq 1$  and  $A_r^{(\nu)} \leq A_{r+1}^{(\nu)}$  if  $p \geq 1$ . Hence in the first case:

$$|I| < n C \cdot A_{n-k}^{(\nu)} \{A_1^{(i)} + \dots + A_k^{(i)}\}$$

or

$$|I| < n C \cdot A_{n-k}^{(\nu)} \cdot A_k^{(i+1)};$$

in the second case:

$$|I| < n C \cdot A_n^{(\nu)} \cdot A_k^{(i+1)}.$$

$$\begin{aligned} II &= A_{k+1}^{(i)} T_{n-k}^{(\nu)} + \dots + A_n^{(i)} T_1^{(\nu)} = A_{k+1}^{(i)} \{T_{n-k}^{(\nu+1)} - T_{n-k-1}^{(\nu+1)}\} + \dots + A_n^{(i)} \{T_1^{(\nu+1)}\} \\ &= A_{k+1}^{(i)} T_{n-k}^{(\nu+1)} + [A_{k+2}^{(i-1)} T_{n-k-1}^{(\nu+1)} + \dots + A_n^{(i-1)} T_1^{(\nu+1)}] \\ &= III + IV. \end{aligned}$$



From  $\frac{S_n^{(p+1)}}{A_n^{(\nu+1)}} \rightarrow s$  it follows that  $\frac{S_n^{(p+2)}}{A_n^{(\nu+2)}} \rightarrow s$ , hence by (1):

$$\frac{1}{n} \cdot \frac{T_n^{(p+1)}}{A_n^{(\nu+1)}} \rightarrow 0.$$

We put  $\left| \frac{T_n^{(p+1)}}{A_n^{(\nu+1)}} \right| = n h_n$ ; then  $\lim_{n \rightarrow \infty} h_n = 0$  and

$$|III| = (n-k) h_{n-k} \cdot A_{k+1}^{(i)} A_{n-k}^{(\nu+1)}$$

$$|IV| \leq h_{n-k-1} \cdot (n-k-1) |A_{k+2}^{(i-1)}| A_{n-k-1}^{(\nu+1)} + \dots + h_1 |A_n^{(i-1)}| A_1^{(\nu+1)}.$$

Hence we have for every  $l$  between 1 and  $n-k+1$ :

$$|IV| \leq [h_{n-k-1}(n-k-1) |A_{k+2}^{(i-1)}| A_{n-k-1}^{(\nu+1)} + \dots + h_{l+1} \cdot (l+1) |A_{n-l}^{(i-1)}| A_{l+1}^{(\nu+1)}] + \\ + [h_l \cdot l \cdot |A_{n-l+1}^{(i-1)}| A_l^{(\nu+1)} + \dots + h_1 |A_n^{(i-1)}| A_1^{(\nu+1)}] = V + VI.$$

Since  $\lim_{n \rightarrow \infty} h_n = 0$  we can find a sequence  $\eta_1 > \eta_2 > \dots$  so that  $h_{n+p} < \eta_p$  and  $\lim_{n \rightarrow \infty} \eta_n = 0$ ; so we have:

$$\frac{V}{n A_n^{(\nu+i)}} < \eta_l \cdot \frac{|A_{k+2}^{(i-1)}| A_{n-k-1}^{(\nu+1)} + \dots + |A_{n-l}^{(i-1)}| A_{l+1}^{(\nu+1)}}{A_n^{(\nu+i)}} \\ < \eta_l \cdot A_{n-k}^{(\nu+1)} \cdot \frac{|A_{k+2}^{(i-1)}| + \dots + |A_{n-l}^{(i-1)}|}{A_n^{(\nu+i)}}.$$

$$|A_{k+2}^{(i-1)}| + \dots + |A_{n-l}^{(i-1)}| = -\{A_{k+2}^{(i-1)} + \dots + A_{n-l}^{(i-1)}\} = -\{A_{n-l}^{(i)} - A_{k+1}^{(i)}\} = \\ = A_{k+1}^{(i)} - A_{n-l}^{(i)} < A_{k+1}^{(i)} < A_k^{(i)}$$

$$\frac{V}{n A_n^{(\nu+i)}} < \eta_l \cdot \frac{A_{n-k}^{(\nu+1)} A_k^{(i)}}{A_n^{(\nu+i)}}$$

$$VI < \eta_1 l [ |A_{n-l+1}^{(i-1)}| A_l^{(\nu+1)} + \dots + |A_n^{(i-1)}| A_1^{(\nu+1)} ]$$

$$< \eta_1 l \cdot A_l^{(\nu+1)} [ -A_{n-l+1}^{(i-1)} - \dots - A_n^{(i-1)} ]$$

$$< \eta_1 l A_l^{(\nu+1)} A_{n-l}^{(i)}.$$

Combining these results we have for every  $k$  between 1 and  $n$  and every  $l$  between 1 and  $n-k+1$  the following inequality:<sup>1)</sup>

<sup>1)</sup> If  $p \leq 1$ , then the first term of the right hand side  $A_n^{(p)}$  must be replaced by  $A_{n-k}^{(p)}$ ; this alteration does not affect the result.

$$\left| \frac{1}{n} \cdot \frac{T_n^{(\nu+i)}}{A_n^{(\nu+i)}} \right| < C \cdot \frac{A_k^{(i+1)} A_n^{(\nu)}}{A_n^{(\nu+i)}} + \eta_{n-k} \cdot \frac{A_{k+1}^{(i)} A_{n-k}^{(\nu+1)}}{A_n^{(\nu+i)}} + \eta_l \cdot \frac{A_{n-k}^{(\nu+1)} A_k^{(i)}}{A_n^{(\nu+i)}} + \eta_1 \cdot \frac{l}{n} \cdot \frac{A_l^{(\nu+1)} A_{n-l}^{(i)}}{A_n^{(\nu+i)}}.$$

Applying the lemma and observing that  $(k+1)^{i-1}$  is less than  $k^{i-1}$  multiplied by a constant independent of  $k$ , we find:

$$\left| \frac{1}{n} \cdot \frac{T_n^{(\nu+i)}}{A_n^{(\nu+i)}} \right| < C' \left[ \frac{k^i n^{\nu-1}}{n^{\nu+i-1}} + \eta_{n-k} \cdot \frac{k^{i-1} (n-k)^\nu}{n^{\nu+i-1}} + \eta_l \cdot \frac{(n-k)^\nu k^{i-1}}{n^{\nu+i-1}} + \eta_1 \cdot \frac{l}{n} \cdot \frac{l^\nu (n-l)^{i-1}}{n^{\nu+i-1}} \right],$$

and, putting  $\frac{k}{n} = r$ ,

$$\left| \frac{1}{n} \cdot \frac{T_n^{(\nu+i)}}{A_n^{(\nu+i)}} \right| < C' \left[ r^i + \eta_{n-k} \cdot r^{i-1} \cdot (1-r)^\nu + \eta_l (1-r)^\nu r^{i-1} + \eta_1 \cdot \left(\frac{l}{n}\right)^{\nu+1} \left(1 - \frac{l}{n}\right)^{i-1} \right].$$

We now prove that the expression between brackets remains less than an arbitrarily chosen positive number  $\epsilon$ , provided  $n$  is taken large enough. For that purpose we first choose  $r$  so small that the first term remains less than  $\frac{\epsilon}{4}$ , and then take  $l$  so large that the third term cannot exceed the same amount. By doing this we have also fixed a lower limit for  $n$ . Now we take  $n$  so large that in the same time the second and the fourth term remain less than  $\frac{\epsilon}{4}$ . This is possible since both terms tend to 0 as  $n \rightarrow \infty$ . Hence our theorem is proved.

## § 2.

We prove that the product of a series, whose index is  $p$ , by a series, which is summable of order  $q$ , need not be summable of order  $p+q+1$ . Consider the series:

$$1 - \left(1 + \frac{1}{2}\right) + \left(1 + \frac{1}{2} + \frac{1}{3}\right) - \dots$$

and

$$\frac{1}{\log 2} - \left[ \frac{1}{\log 2} + \frac{1}{\log 3} \right] + \left[ \frac{1}{\log 3} + \frac{1}{\log 4} \right] - \dots$$

The index of the first series is zero, and its sum is  $\frac{1}{2} \log 2^1$ ; the other converges to zero and is therefore summable of order zero. We prove that their product is not summable of order  $0 + 0 + 1$ . We have<sup>1)</sup>:

$$\begin{aligned} W_n^{(2)} &= s_1 t_n + s_2 t_{n-1} + \dots + s_n t_1 = \frac{(-1)^{n+1}}{\log(n+1)} \cdot 1 + \frac{(-1)^n}{\log n} \left\{ -\frac{1}{2} \right\} + \\ &\quad + \frac{(-1)^{n-1}}{\log(n-1)} \left\{ 1 + \frac{1}{3} \right\} + \dots \\ &= (-1)^{n+1} \left[ \frac{1}{\log(n+1)} + \frac{1}{2} \cdot \frac{1}{\log n} + \left( 1 + \frac{1}{3} \right) \cdot \frac{1}{\log(n-1)} + \dots \right]. \end{aligned}$$

Hence:

$$\left| W_n^{(2)} \right| > \frac{1}{\log(n+1)} \left[ 1 + \left( \frac{1}{2} \right) + \left( 1 + \frac{1}{3} \right) + \left( \frac{1}{2} + \frac{1}{4} \right) + \left( 1 + \frac{1}{3} + \frac{1}{5} \right) + \dots \right]$$

where the last term of the expression between brackets amounts

$$1 + \frac{1}{3} + \frac{1}{5} + \dots + \frac{1}{n} \quad \text{or} \quad \frac{1}{2} + \frac{1}{4} + \dots + \frac{1}{n}.$$

Therefore:

$$\begin{aligned} \left| W_n^{(2)} \right| &> \frac{1}{\log(n+1)} \left[ \frac{n}{2} \cdot 1 + \left( \frac{n}{2} - 1 \right) \cdot \frac{1}{2} + \left( \frac{n}{2} - 1 \right) \cdot \frac{1}{3} + \right. \\ &\quad \left. + \left( \frac{n}{2} - 2 \right) \cdot \frac{1}{4} + \dots + \left( \frac{n}{2} - \frac{n-2}{2} \right) \cdot \frac{1}{n} \right], \end{aligned}$$

$$\begin{aligned} \left| W_n^{(2)} \right| &> \frac{1}{\log(n+1)} \left[ \frac{n}{2} \left( 1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n} \right) - \right. \\ &\quad \left. - \left( \frac{1}{2} + \frac{1}{3} + \frac{2}{4} + \frac{2}{5} + \dots + \frac{n-2}{2(n-1)} \right) \right] \end{aligned}$$

or, since  $1 + \frac{1}{2} + \dots + \frac{1}{p} > \log p$ ,

$$\left| W_n^{(2)} \right| > \frac{n \log(n-1)}{2 \log(n+1)} - \frac{n-1}{2 \log(n+1)},$$

hence

$$\frac{1}{n} \left| W_n^{(2)} \right| > \frac{1}{2} \left\{ \frac{\log(n-1)}{\log(n+1)} - \frac{1}{\log(n+1)} \right\}.$$

<sup>1)</sup> See these Proceedings, Vol. XXVII, p. 690, 691.

<sup>2)</sup> For the notation, see these Proceedings, Vol. XXVI, p. 204, 205.

But:

$$\lim_{n \rightarrow \infty} \frac{1}{2} \left\{ \frac{\log(n-1)}{\log(n+1)} - \frac{1}{\log(n+1)} \right\} = \frac{1}{2}.$$

Consequently we can find an integer  $m$  so that  $\frac{W_n^{(2)}}{n} > \frac{1}{3}$  for  $n > m$ . Since the summability of order 1 of the product-series implies that  $\frac{W_n^{(2)}}{n}$  for  $n \rightarrow \infty$  tends to the product of the sums of the two series, in casu to zero, it is clear that our product series cannot be summable of order 1.

#### REMARK.

The proof in § 1 is wholly analogous to the proof which HARDY and LITTLEWOOD have given for their theorem that every convergent series whose terms satisfy the relation  $|na_n| < k$  has an index equal to  $-1$ <sup>1)</sup>. Hence we are inclined to call such series joinable of order zero: however these series may lack the important property of joinable series mentioned at the beginning of this article<sup>2)</sup>: therefore such a nomenclature would not be very consequent. From the theorem of § 1 however it is clear that it is also less desirable to call the absolute convergent series joinable of order zero, as has been done in our previous article: indeed a series which is joinable of order  $p > 0$  is summable of any order  $> p - 1$  while an absolute convergent series (which we have called joinable of order zero) need not even be summable of order  $-\frac{1}{2}$ <sup>3)</sup>.

To remain consequent, we may only call those series joinable of order zero, whose terms (except the first) consist of mere zeros<sup>4)</sup>.

<sup>1)</sup> *Contributions to the Arithmetic Theory of Series*. Proc. Lond. Math. Soc., Ser. 2 Vol. 11, p. 462, 463.

<sup>2)</sup> For an example, see these Proceedings, Vol. XXVII, p. 38.

<sup>3)</sup> Cf. S. CHAPMAN, *Non-integral orders of summability of series and integrals*. Proc. Lond. Math. Soc., Ser. 2, Vol. 9, p. 398.

<sup>4)</sup> This may be deduced from the property that the mean values of order  $p + i - 1$  of a series which is joinable of order  $p$  ( $p > 0$ ) are uniformly limited for  $i > 0$ . Cf. these Proceedings, Vol. XXVII, p. 692.



**Mathematics.** — “*Ueber projektive Differentialinvarianten.*” II.  
Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of December 27, 1924).

In einer ersten Mitteilung wurde gezeigt, wie man aus  $m + 2$  projektiven Differentialinvarianten  $K_1, K_2, \dots, K_{m+2}$  eines Punktes

$$y_i = y_i(t_1, t_2, \dots, t_m) \quad (i = 1, 2, \dots, n), n \geq m + 2, m \geq 1 \quad (1)$$

einer  $m$ -dimensionalen  $t$ -Mannigfaltigkeit  $R_m$  eine weitere Differentialinvariante

$$J = \{K_1, K_2, \dots, K_{m+2}\} \quad (2)$$

ableiten kann. Dabei sind die Klammerausdrücke  $\{K_1, K_2, \dots, K_{m+2}\}$  gegeben durch die  $m + 2$ -reihige Determinante

$$J = \begin{vmatrix} q_1 K_1 & q_2 K_2 & \dots & q_{m+2} K_{m+2} \\ p_1 K_1 & p_2 K_2 & \dots & p_{m+2} K_{m+2} \\ \frac{\partial K_1}{\partial t_1} & \frac{\partial K_2}{\partial t_1} & \dots & \frac{\partial K_{m+2}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_1}{\partial t_m} & \frac{\partial K_2}{\partial t_m} & \dots & \frac{\partial K_{m+2}}{\partial t_m} \end{vmatrix} \quad (3)$$

$q_i$  ist das  $\Delta$ -Gewicht,  $p_i$  das  $\lambda$ -Gewicht von  $K_i$ . Die Ordnung von  $J$  ist um eine Einheit grösser als die höchste Ordnung eines  $K_i$ .

Es scheint nun, dass die Verwendung dieses Satzes zur Erzeugung weiterer Differentialinvarianten das Bekanntsein von wenigstens  $m + 2$  Invarianten voraussetzt. Wir zeigen hier, dass dies nicht der Fall ist und dass man schon mit zwei relativen Invarianten auskommt.

Diese zwei Invarianten sind von vorneherein geometrisch gegeben durch den Punkt  $y$  selbst und durch den Tangential- $T_m$  in  $y$ .

Wir bemerken noch, dass diese Methode auch z.B. bei affinen Differentialinvarianten anwendbar ist; an Stelle von (3) tritt dann die durch (24) der ersten Mitteilung gegebene Determinante von  $m + 1$  Reihen.

### § 1.

Sind  $u_i$  veränderliche Koordinaten eines linearen,  $(n - 2)$ -dimensionalen Raumes, dann ist

$$U = (u'y) = u'_1 y_1 + u'_2 y_2 + \dots + u'_n y_n = 0 \quad (4)$$

die Gleichung des Punktes  $y$ . Die Invariante  $U$  hat die Ordnung Nul; ihr  $\Delta$ -Gewicht ist ebenfalls Nul, ihr  $\lambda$ -Gewicht ist 1.

Sind

$$\pi_{i_1 i_2 \dots i_{n-m-1}} = \pi'_{k_1 k_2 \dots k_{m+1}}$$

die Koordinaten eines veränderlichen, linearen  $(n-2-m)$ -dimensionalen Raumes, dann ist

$$\sum \pi'_{k_1 k_2 \dots k_{m+1}} (y y_{t_1} y_{t_2} \dots y_{t_m})_{k_1 k_2 \dots k_{m+1}} = 0 \dots (5a)$$

oder

$$\sum \pi_{i_1 i_2 \dots i_{n-m-1}} (y y_{t_1} y_{t_2} \dots y_{t_m})_{i_1 i_2 \dots i_{n-m-1}} = 0 \dots (5b)$$

die Gleichung des Tangential- $R_m$  im Punkte  $y$ . Dabei sind die Indexgruppen  $i_1 i_2 \dots i_{n-m-1}$  und  $k_1 k_2 \dots k_{m+1}$  algebraisch-complementär und  $(y y_{t_1} y_{t_2} \dots y_{t_m})_{k_1 k_2 \dots k_{m+1}}$  ist eine  $(m+1)$ -reihige Determinante aus der Matrix:

$$\left| \begin{array}{cccccc} y_1 & y_2 & \dots & \dots & \dots & y_n \\ \frac{\partial y_1}{\partial t_1} & \frac{\partial y_2}{\partial t_1} & \dots & \dots & \dots & \frac{\partial y_n}{\partial t_1} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \frac{\partial y_1}{\partial t_m} & \frac{\partial y_2}{\partial t_m} & \dots & \dots & \dots & \frac{\partial y_n}{\partial t_m} \end{array} \right|$$

Wir setzen voraus, dass nicht alle diese Determinanten Nul sind, dass also der Tangentialraum existiert.

Verwenden wir Komplexsymbole, so können wir statt (5) etwas kürzer schreiben:

$$\Pi = (\pi^{n-m-1} y y_{t_1} y_{t_2} \dots y_{t_m}) = (n-m-1)! (\pi' y) (\pi' y_{t_1}) \dots (\pi' y_{t_m}) = 0 \dots (6)$$

Die Invariante  $\Pi$  ist von erster Ordnung und hat das  $\Delta$ -Gewicht 1, das  $\lambda$ -Gewicht  $m+1$ .

Es bedeute nun  $s$  eine der Zahlen  $1, 2, \dots, m$ . Wir wählen  $s$  untereinander and mit  $u'$  cogrediente Reihen

$$u'_{(h)} = (u'_{(h)1}, u'_{(h)2}, \dots, u'_{(h)n}) \quad (h = 1, 2, \dots, s) \dots (7)$$

und  $m+2-s$  untereinander und mit  $\pi_{i_1 i_2 \dots i_{n-m-1}}$  cogrediente Reihen

$$(\pi_{(k)})_{i_1 i_2 \dots i_{n-m-1}} \quad (k = 1, 2, \dots, m+2-s) \dots (8)$$

und bilden mit diesen Reihen analog zu (4) und (6) die  $s$  Invarianten

$$U_{(h)} = (u'_{(h)} y) \quad (h = 1, 2, \dots, s) \dots (9)$$

und die  $m+2-s$  Invarianten

$$\Pi_{(k)} = (\pi_{(k)}^{n-m-1} y y_{t_1} y_{t_2} \dots y_{t_m}) \quad (k=1, 2, \dots, m+2-s) \quad (10)$$

Dies sind zusammen  $s + (m+2-s) = m+2$  Invarianten, die wir an Stelle der  $K_i$  in (3) verwenden. Wir bekommen so die folgende Differentialinvariante zweiter Ordnung:

$$J_s = \begin{array}{c} \begin{array}{ccccc} & \overbrace{\hspace{1.5cm}}^s & & \overbrace{\hspace{1.5cm}}^{m+2-s} & \\ 0 & \dots & 0 & \Pi_{(1)} \dots & \Pi_{(m+2-s)} \\ (u'_{(1)} y) \dots (u'_{(s)} y) & & (m+1) \Pi_{(1)} \dots & (m+1) \Pi_{(m+2-s)} \\ (u'_{(1)} y_{t_1}) \dots (u'_{(s)} y_{t_1}) & & \frac{\partial \Pi_{(1)}}{\partial t_1} \dots & \frac{\partial \Pi_{(m+2-s)}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ (u'_{(1)} y_{t_m}) \dots (u'_{(s)} y_{t_m}) & & \frac{\partial \Pi_{(1)}}{\partial t_m} \dots & \frac{\partial \Pi_{(m+2-s)}}{\partial t_m} \end{array} \end{array} \quad \dots (11)$$

Wie sofort zu sehen, bekommen wir bei  $s=m+1$  keine neue Invariante; denn dann stehen in der ersten Zeile in (11) lauter Nullen bis auf das letzte Element  $\Pi_{(1)}$ .  $J_{m+1}$  ist dann gleich dem Produkte von  $\Pi_{(1)}$  und der Determinante

$$\begin{vmatrix} (u'_{(1)} y) & (u'_{(2)} y) & \dots & (u'_{(m+1)} y) \\ (u'_{(1)} y_{t_1}) & (u'_{(2)} y_{t_1}) & \dots & (u'_{(m+1)} y_{t_1}) \\ \dots & \dots & \dots & \dots \\ (u'_{(1)} y_{t_m}) & (u'_{(2)} y_{t_m}) & \dots & (u'_{(m+1)} y_{t_m}) \end{vmatrix} \quad \dots (12)$$

die durch die Substitution

$$\pi'_{k_1 k_2 \dots k_{m+1}} = (u'_{(1)} u'_{(2)} \dots u'_{(m+1)})_{k_1 k_2 \dots k_{m+1}} \quad \dots (13)$$

aus (6) entsteht.

Hingegen erhalten wir beim Grenzfall  $s=1$  eine Invariante zweiter Ordnung, bei der sich der Faktor  $(u'_{(1)} y)$  abspalten lässt. Wir haben nämlich bei  $s+1$  in (11) die zwei ersten Zeilen

$$\begin{array}{ccccccc} 0 & & \Pi_{(1)} & \dots & \dots & & \Pi_{(m+1)} \\ (u' y) & (m+1) \Pi_{(1)} & \dots & \dots & \dots & (m+1) \Pi_{(m+1)} & \end{array}$$

und die Entwicklung nach diesen beiden Zeilen gibt  $J_1 = (u' y) \cdot K$ , wo  $K$  die  $(m+1)$ -reihige Determinante ist:

$$K = \begin{vmatrix} \Pi_{(1)} & \Pi_{(1)} & . & . & . & \Pi_{(m+1)} \\ \frac{\partial \Pi_{(1)}}{\partial t_1} & \frac{\partial \Pi_{(2)}}{\partial t_1} & . & . & . & \frac{\partial \Pi_{(m+1)}}{\partial t_1} \\ . & . & . & . & . & . \\ \frac{\partial \Pi_{(1)}}{\partial t_m} & \frac{\partial \Pi_{(2)}}{\partial t_m} & . & . & . & \frac{\partial \Pi_{(m+1)}}{\partial t_m} \end{vmatrix} \quad . \quad . \quad . \quad (14)$$

## § 2.

Es sei  $m \geq 1$  fest gegeben. Wir betrachten die im vorigen § ausinandergesetzte Konstruktion von  $J$  in erster Linie für  $n = m + 2$ , also für eine  $m$ -dimensionale Hyperfläche  $R_m$  in einem projektiven Raum  $G_{m+1}$  von  $m + 1$  Dimensionen. Man kann nämlich, so wie wir in diesem §. zeigen wollen, aus Differentialinvarianten einer  $R_m$  in  $G_{m+1}$  solche einer  $R_m$  in einem  $G_{m+1+k}$  ( $k \geq 1$ ) mit Hilfe eines "Uebertragungsprinzipes" finden.

Sei  $f$  eine Differentialinvariante einer  $R_m$  in  $G_{m+1}$ .  $f$  ist ein Polynom von Faktoren erster Art  $\varphi_1$  und von Faktoren zweiter Art  $\varphi_2$ :

$$\left. \begin{aligned} \varphi_1' &= (u' y_\alpha) \quad , \quad \varphi_1'' = (u' \xi) \\ \varphi_2' &= (y_\alpha y_\beta \dots \xi \eta \dots \zeta) \quad , \quad \varphi_2'' = (u' v' \dots w') \end{aligned} \right\} \quad . \quad . \quad (15)$$

$f$  ist homogen bezgl. jeder der Reihen  $y_\alpha, \xi, \dots; u', v', \dots, w'$ .

Wir formen nun  $f$  so um, dass der neue Ausdruck ausschliesslich aus Faktoren  $\varphi_1'$  aufgebaut ist. Das geht z. B. folgendermassen. Enthält  $f$  Reihen  $\pi'_{ikl} \dots$  oder  $\pi_{ikl} \dots$ , dann führen wir an deren Stelle mit Hilfe einer mit (13) analogen Substitution Reihen  $u', v', \dots$  bzw.  $\xi, \eta, \dots$  ein. Hiedurch entstehe  $f'$ . Von  $f'$  bilden wir Polaren  $f''$ , die die Reihen  $u', v', \dots$  nur linear enthalten. Schliesslich ersetzen wir jede Reihe  $u'$  durch

$$u_{i_1 i_2 \dots i_{n-1}} = u_{i_1} u_{i_2} \dots u_{i_{n-1}}$$

wo nun die  $u_i$   $(n-1)$ -fältige Komplexsymbole sind. Hiedurch wird

$$(u' \xi) = \frac{1}{(n-1)!} (u^{n-1} \xi); \quad . \quad . \quad . \quad (16)$$

dagegen wird:

$$(u' v' \dots w') = (u v) \dots (u w) = \left( \frac{1}{(n-1)!} \right)^{n-1} (v^{n-1} u) \dots (w^{n-1} u). \quad (17)$$



Aus  $f''$  entsteht auf diese Weise  $f'''$  und schreiben wir hiefür wieder  $f$ , dann enthält  $f$  ausschliesslich Klammerfaktoren

$$\varphi'_2 = (y_\alpha y_\beta \dots \xi \eta \dots \xi).$$

„Erweitern“ wir nun jeden dieser Faktoren, d.h. schreiben wir statt  $\varphi'_2$  den  $(m+1+k)$ -dimensionalen Klammerfaktor

$$\Phi'_2 = (y_\alpha y_\beta \dots \xi \eta \dots \xi \xi_{(1)} \xi_{(2)} \dots \xi_{(k)}) \dots \dots \dots, \quad (18)$$

dann entsteht aus  $f$  eine Differentialinvariante  $F$  derselben Ordnung einer  $R_m$  im  $G_{m+1+k}$ . Denn jedes  $\Phi'_2$  ist in diesem Raume  $G_{m+1+k}$  eine projektive Invariante, also auch  $F$  selbst. Und gegenüber den beiden Transformationen

$$t_i = t_i(\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m) \quad \bar{y}_i = \lambda y_i$$

hat sich nichts geändert.

Wir beleuchten dieses „Uebertragungsprinzip“ durch zwei einfache Beispiele.

1.  $m=1, k=1$ . In der Ebene haben wir im Punkte  $y$  einer Kurve z. B. die Differentialinvariante

$$f = (y y' y'').$$

Hieraus finden wir:

$$F = (y y' y'' \xi)$$

als Differentialinvariante einer Raumkurve. ( $F=0$  gibt die Osculationsebene).

2.  $m=2, k=1$ . In dreidimensionalen  $G_3$  hat eine Fläche

$$y_i = y_i(u, v) \quad (i=1, 2, 3, 4)$$

die Differentialinvariante zweiter Ordnung

$$f = (y y_u y_v y_{uu}) (y y_u y_v y_{vv}) - (y y_u y_v y_{uv})^2.$$

Hieraus finden wir im vierdimensionalen Raume  $G_4$ :

$$F = (y y_u y_v y_{uu} \xi) (y y_u y_v y_{vv} \xi) - (y y_u y_v y_{uv} \xi)^2.$$

Hier gibt  $F=0$  bei veränderlichen  $\xi_i$  die beiden dreidimensionalen Räume, die durch die Tagentialebene  $(\pi^2 y y_u y_v) = 0$  gehen und die  $R_2$  nach Kurven schneiden, die in  $y$  einen Doppelpunkt mit zusammenfallenden Tangenten besitzen.

### § 3.

Ist jetzt  $n = m+2$ , dann haben wir an Stelle von (6)

$$\Pi = (x y y_{t_1} y_{t_2} \dots y_{t_m}) = (x v') = (v' x) = 0 \dots \dots (19)$$

als Gleichung des  $m$ -dimensionalen Tangentialraumes im Punkte  $y$ . Die durch (11) gegebene Invariante hat dann die Gestalt

$$J_s = \begin{vmatrix} \overbrace{0 \quad \dots \quad 0}^s & \overbrace{(x_{(1)} v') \dots (x_{(m+2-s)} v')}^{m+2-s} \\ (u'_{(1)} y) \dots (y'_{(s)} y) & (m+1)(x_{(1)} v') \dots (m+1)(x'_{(m+2-s)} v') \\ \dots & \dots \\ (u'_{(1)} y_{t_m}) \dots (u'_{(s)} y_{t_m}) & (x_{(1)} v'_{t_m}) \dots (x_{(m+2-s)} v'_{t_m}) \end{vmatrix} \quad (20)$$

Hier können wir z.B. alle  $s$  Reihen  $u'_{(i)}$  ersetzen durch  $\pi'$ , wo die  $\pi'_i$   $s$ -fältige Komplexsymbole sind und ebenso alle  $m+2-s$  Reihen  $x_{(i)}$  ersetzen durch  $\varrho$ , wo die  $\varrho$   $(m+2-s)$ -fältige Komplexsymbole bedeuten.

Aus (20) entsteht dann:

$$J_s = \begin{vmatrix} \overbrace{0 \quad \dots \quad 0}^s & \overbrace{(\varrho v') \dots (\varrho v')}^{m+2-s} \\ (\pi' y) \dots (\pi' y) & (m+1)(\varrho v') \dots (m+1)(\varrho v') \\ (\pi' y_{t_1}) \dots (\pi' y_{t_1}) & (\varrho v'_{t_1}) \dots (\varrho v'_{t_1}) \\ \dots & \dots \\ (\pi' y_{t_m}) \dots (\pi' y_{t_m}) & (\varrho v'_{t_m}) \dots (\varrho v'_{t_m}) \end{vmatrix} \quad (21)$$

Ist hier

$$\pi'_{i_1 i_2 \dots i_s} = \varrho'_{i_1 i_2 \dots i_s},$$

dann gibt  $J_s = 0$  einen quadratischen Komplex  $\Omega_s$  von  $(m+1-s)$ -dimensionalen Räumen; bei  $s=m$  also einen quadratischen Linienkomplex.

Der Grenzfall  $s=1$  gibt hier, genau so wie in § 1  $J_1 = (u' y) \cdot K$  und  $K$  lässt sich mit Hilfe von Komplexsymbolen analog zu (21) wie folgt ausdrücken:

$$K = \begin{vmatrix} (\varrho v') & (\varrho v') & \dots & (\varrho v') \\ (\varrho v'_{t_1}) & (\varrho v'_{t_1}) & \dots & (\varrho v'_{t_1}) \\ \dots & \dots & \dots & \dots \\ (\varrho v'_{t_m}) & (\varrho v'_{t_m}) & \dots & (\varrho v'_{t_m}) \end{vmatrix} = (\varrho' v'_{t_1} \dots v'_{t_m}) \quad (22)$$

Vom Vorzeichen abgesehen ist also, wenn wir  $q' = u'$  setzen:

$$K = \sum (u' v'_{t_1} \dots v'_{t_m})_{i_1 \dots i_{m+1}} (y y_{t_1} \dots y_{t_m})_{i_1 \dots i_{m+1}},$$

$$K = \begin{vmatrix} (u' y) & (u' y_{t_1}) & \dots & (u' y_{t_m}) \\ (v'_{t_1} y) & (v'_{t_1} y_{t_1}) & \dots & (v'_{t_1} y_{t_m}) \\ \dots & \dots & \dots & \dots \\ (v'_{t_m} y) & (v'_{t_m} y_{t_1}) & \dots & (v'_{t_m} y_{t_m}) \end{vmatrix} \quad (23)$$

Wegen

$$(v'_{t_1} y) = (v'_{t_2} y) = \dots = (v'_{t_m} y) = 0$$

haben wir also

$$K = (-1)^m \cdot (u' y) \cdot A \quad (24)$$

wobei nun die Differentialinvariante zweiter ordnung  $A$  gegeben wird durch

$$A = (-1)^m \cdot | (v'_{t_i} y_{t_k}) | \quad (25)$$

Da weiters wegen (19)

$$v'_{t_i} = (y y_{t_1 t_i} y_{t_2} \dots y_{t_m}) + (y y_{t_1} y_{t_2 t_i} \dots y_{t_m}) + \dots + (y y_{t_1} \dots y_{t_{m-1} t_i} y_{t_m}) \quad (26)$$

ist, wird:

$$(v'_{t_i} y_{t_k}) = (y_{t_k} y y_{t_1} \dots y_{t_{i-1} t_i} \dots y_{t_m}) = - (y_{t_i t_k} y y_{t_1} \dots y_{t_m}) = - (v' y_{t_i t_k}). \quad (27)$$

Wir haben daher auch:

$$A = (-1)^m \cdot | (v'_{t_i} y_{t_k}) | = | (y_{t_i t_k} y y_{t_1} \dots y_{t_m}) | = | (y_{t_i t_k} v') | \quad (28)$$

$A$  ist demnach nichts anderes als die Discriminante der sogen. ersten (projektiven) Differentialform  $F_s$  der Hyperfläche  $R_m$ .

$$F_s = \sum (y y_{t_1} \dots y_{t_m} y_{t_i t_k}) dt^i dt^k \quad (29)$$

$A$  hat das  $\Delta$ -Gewicht  $m + 2$  und das  $\lambda$ -Gewicht  $m(m + 2)$ .

#### § 4.

Wir wollen jetzt noch zeigen, dass durch  $J_s = 0$  (Vgl. (21)), die Gleichung des quadratischen,  $(m - 1)$ -dimensionalen Asymptotenkegels mit der Spitze  $y$  in veränderlichen  $R_{m+1-s}$ -Koordinaten

$$\pi_{i_1 i_2 \dots i_{m+2-s}} = \varphi_{i_1 i_2 \dots i_{m+2-s}} = \pi'_{k_1 k_2 \dots k_s} = \varphi'_{k_1 k_2 \dots k_s}$$

dargestellt wird.

Hierzu entwickeln wir die Determinant  $J_s$  nach LAPLACE, indem wir die ersten  $s$  Kolonnen zusammenfassen. Schreiben wir dann

noch  $y_i$  an Stelle von  $y_{t_i} = \frac{\partial y}{\partial t_i}$  und  $v_i'$  an Stelle von  $v'_{t_i} = \frac{\partial v}{\partial t_i}$ ,

dann haben wir, wenn  $c \neq 0$  einen Zahlenfaktor bedeutet:

$$c J_s = \sum_{(i,k)} (\pi^{m+2-s} y y_{i_1} y_{i_2} \dots y_{i_{s-1}}) (q'^s v' v'_{k_1} v'_{k_2} \dots v'_{k_{m+1-s}}), \quad (30)$$

Hier sind die zwei Indexgruppen  $i_1 i_2 \dots i_{s-1}$  und  $k_1 k_2 \dots k_{m+1-s}$  algebraisch-komplementär bezüglich aller Ziffern  $1 2 \dots m$  und die Summe wird erstreckt über alle

$$\binom{m}{s-1} = \binom{m}{m+1-s}$$

Kombinationen  $i_1 i_2 \dots i_{s-1}$ .

In (30) formen wir durch Einführung von  $v' = (y y_1 y_2 \dots y_m)$  den zweiten Klammerfaktor um:

$$\begin{aligned} & \sum_v (q'^s v'_{k_1} v'_{k_2} \dots v'_{k_{m+1-s}})_{v_1 v_2 \dots v_{m+1}} \cdot (y y_1 y_2 \dots y_m)_{v_1 v_2 \dots v_{m+1}} = \\ & = \left| \begin{array}{cccc} (q' y) & (q' y_1) & \dots & (q' y_m) \\ & \dots & \dots & \dots \\ (q' y) & (q' y_1) & \dots & (q' y_m) \\ 0 & (v'_{k_1} y_1) & \dots & (v'_{k_1} y_m) \\ & \dots & \dots & \dots \\ 0 & (v'_{k_{m+1-s}} y_1) & \dots & (v'_{k_{m+1-s}} y_m) \end{array} \right| \begin{array}{l} \left. \vphantom{\begin{array}{c} (q' y) \\ \dots \\ (q' y) \end{array}} \right\} s \\ \left. \vphantom{\begin{array}{c} (v'_{k_1} y_1) \\ \dots \\ (v'_{k_{m+1-s}} y_1) \end{array}} \right\} m+1-s \end{array} \end{aligned}$$

oder, wenn wir die ersten  $s$  Reihen zusammenfassen:

$$\begin{aligned} & (q'^s v' v'_{k_1} \dots v'_{k_{m+1-s}}) = \\ & = c' \cdot \sum_{(\alpha, \beta)} (\pi^{m+2-s} y y_{\alpha_1} \dots y_{\alpha_{s-1}}) \cdot \left| \begin{array}{cccc} (v'_{k_1} y_{\beta_1}) & \dots & (v'_{k_1} y_{\beta_{m+1-s}}) \\ & \dots & \dots & \dots \\ & \dots & \dots & \dots \\ (v'_{k_{m+1-s}} y_{\beta_1}) & \dots & (v'_{k_{m+1-s}} y_{\beta_{m+1-s}}) \end{array} \right| \quad (31) \end{aligned}$$

Hier sind wieder  $\alpha_1 \alpha_2 \dots \alpha_{s-1}$  und  $\beta_1 \beta_2 \dots \beta_{m+1-s}$  algebraisch-komplementär.

Aus (30) wird dann:

$$c'' \cdot J = \sum_{(i,k)} \sum_{(\alpha, \beta)} (\pi^{m+2-s} y y_{i_1} \dots y_{i_{s-1}}) (q^{m+2-s} y y_{\alpha_1} \dots y_{\alpha_{s-1}}) \mathfrak{A}_{\beta_1 \beta_2 \dots \beta_{m+1-s}}^{k_1 k_2 \dots k_{m+1-s}} \quad (32)$$

wo  $\mathfrak{A}$  einen Minor mit  $m+1-s$  Reihen aus (25) bedeutet.

Ein veränderlicher, linearer  $R_{m+1-s}$  mit den Koordinaten  $\pi_{i_1 i_2 \dots i_{m+2-s}}$  schneidet den Tangentialraum  $T_m$  nach einem linearen Raum  $S_{m-s}$ .



Nehmen wir die  $m+1$  Punkte  $y, y_1, \dots, y_m$  als Grundpunkte im  $T_m$ , dann ist ein Punkt  $\xi_{(j)}$  in  $T_m$  gegeben durch

$$\xi^{(j)} = \lambda_0^{(j)} y + \lambda_1^{(j)} y_1 + \dots + \lambda_m^{(j)} y_m \quad (33)$$

Dabei können wir  $\lambda_0^{(j)}, \lambda_1^{(j)}, \dots, \lambda_m^{(j)}$  als Koordinaten von  $\xi^{(j)}$  bezgl. des Simplex  $y, y_1, \dots, y_m$  betrachten. Sei nun  $j = 1, 2, \dots, m+1-s$  und sei  $S_{m-s}$  bestimmt durch die  $m+1-s$  Punkte  $\xi_{(j)}$ . Ist dann  $\eta$  ein nicht im  $T_m$  gelegener Punkt des Raumes  $R_{m+1-s}(\pi_{i_1 i_2} \dots i_{m+2-s})$ , dann kann man setzen ( $c \neq 0$ ):

$$c(\pi^{m+2-s} y y_{i_1} \dots y_{i_{s-1}}) = (\eta \xi^{(1)} \xi^{(2)} \dots \xi^{(m+1-s)} y y_{i_1} \dots y_{i_{s-1}}),$$

oder, wenn wir (33) berücksichtigen:

$$c'(\pi^{m+2-s} y y_{i_1} \dots y_{i_{s-1}}) = (\eta y y_1 y_2 \dots y_m) \cdot (\lambda^{(1)} \lambda^{(2)} \dots \lambda^{(m+1-s)})_{k_1 k_2 \dots k_{m+1-s}} \quad (34)$$

Hier ist  $(\eta y y_1 \dots y_m) \neq 0$  und

$$P_{k_1 k_2 \dots k_{m+1-s}} = (\lambda^{(1)} \lambda^{(2)} \dots \lambda^{(m+1-s)})_{k_1 k_2 \dots k_{m+1-s}} = P'_{i_1 i_2 \dots i_{s-1}} \quad (35)$$

sind die Koordinaten des  $S_{m-s}$  im  $T_m$  bezgl. des Simplex  $y, y_1, \dots, y_m$ .

Nach (32) wird also  $J=0$  gleichbedeutend mit

$$\sum_{(i,k)} \sum_{(\alpha, \beta)} P'_{i_1 i_2 \dots i_{s-1}} Q'_{\alpha_1 \alpha_2 \dots \alpha_{s-1}} \eta_{\beta_1 \beta_2 \dots \beta_{m+1-s}}^{k_1 k_2 \dots k_{m+1-s}} = 0 \quad (36)$$

und dies ist die Gleichung des Asymptotenkegels

$$\sum (y y_1 \dots y_m y_i k) \lambda_i \lambda_k = 0 \quad (37)$$

in  $R_{m+2-s}$ -Koordinaten (Vgl. (29)).

Wir merken noch an, dass man (32) mit Hilfe einer  $(m+s+1)$ -reihigen Determinante kann ausdrücken:

$$J = \begin{vmatrix} (v'_1 y_1) & \dots & (v'_1 y_m) & 0 & (\pi' y_1) & \dots & (\pi' y_1) \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ (v'_m y_1) & \dots & (v'_m y_m) & 0 & (\pi' y_m) & \dots & (\pi' y_m) \\ 0 & \dots & 0 & 0 & (\pi' y) & \dots & (\pi' y) \\ (\pi' y_1) & \dots & (\pi' y_m) & (\pi' y) & 0 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ (\pi' y_1) & \dots & (\pi' y_m) & (\pi' y) & 0 & \dots & 0 \end{vmatrix} \quad (38)$$

$\underbrace{\hspace{10em}}_m \quad \underbrace{\hspace{10em}}_s$

**Physics.** — *“Accuracy and Sensitiveness of a Pressure Balance Based on a So-Called Amagat Cylinder.”* By A. MICHELS. (14<sup>th</sup> communication of results obtained in researches for the VAN DER WAAALS-fund). (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of June 28, 1924.)

Somewhat less than a year ago<sup>1)</sup> a communication could be made about the causes to which it is due that the sensitiveness of a pressure balance increases so greatly when the piston is set rotating. The researches were continued, now with the intention of obtaining more numerical results.

First the sensitiveness and the accuracy of adjustment could be determined of a pressure balance that was at our disposal (type *S* and *B*) up to 250 atm. For this purpose a tube with platinum contacts of the same type as is used for the determination of isotherms<sup>2)</sup>, was filled with hydrogen gas, put under pressure, and the position of the same contact was determined by means of the pressure balance several times in succession. In the following lines we shall call this apparatus briefly the hydrogen manometer.

In the determination of the contacts care had to be taken that always a uniformly increasing load was worked with. In order to attain this a cylindrical trough was mounted on the axis of the balance, which trough was slowly filled with oil. At the very moment the contact was formed, an electrical tap stopped the oil-supply.

As result we may state that the sensitiveness appeared to be independent of the pressure. Up to the highest load, in our case 250 kg., an accuracy of adjustment of one and a half grams was found. Just as we had expected, the position of the piston proved to play a part, though an insignificant one. This influence is the result of a slight conic shape of the piston, which causes a different effective diameter for each different position. Hence in pressure measurements it deserves recommendation to determine the level of the piston, and to apply a correction for this. There also appeared to be a temperature function. This, however, is entirely to be considered

<sup>1)</sup> These Proceedings, 26, p. 805.

<sup>2)</sup> KOHNSTAMM and WALSTRA, Hydrogen Isotherms. These Proc. 17, p. 203.

as a surface aerial-dilatation of the diameter of the piston. Its influence therefore, can be found by a simple numerical calculation in every observation.

The second task we had set ourselves was to try and solve the question what is to be understood by the effective diameter of the piston. Is the cross-section of the piston itself to be taken for this, or of the hole in which it rotates, or perhaps a value between them?

We first tried to find experimentally the numerical value of the effective diameter and its dependence on the pressure, if existing. For this purpose the position of the same contact in the hydrogen manometer was determined in two different ways. First the hydrogen manometer was directly connected with the pressure balance, and the position of a contact was determined. Then the pressure balance was connected with a *U*-shaped tube, which was half filled with mercury. The second leg of the *U*-tube was in communication with the hydrogen manometer. The pressure in the manometer could now be taken equal to the pressure exerted by the pressure balance, hence  $\frac{\text{load}}{\text{effective diameter}}$  diminished by the difference of level of the mercury in the two legs.

If however the contact is made, the pressure in the manometer is equal to that obtained in the direct measurement through the balance. From the data obtained in this way the effective diameter may be calculated in an elementary way.

In order to determine the position of the mercury in the *U*-tube, the upper- and the lower-end of this tube partly consisted of a glass-capillary in which the menisci were clearly visible. At the moment of contact in the hydrogen manometer the two mercury levels and a scale division behind them were photographed in order to ascertain their position.

The accuracy of this method is limited by the admissible height of the mercury column. In our case it was about 4.80 m., which corresponds to a pressure of about 6 kg. per cm<sup>2</sup>. In this way an accuracy of measurement of 1/2400 could be attained. Within this limit the effective diameter appeared to be no pressure-function. For want of space we cannot afford to enter more fully into the different corrections to be applied. For a full discussion we may refer to the *Ann. d. Physik Bd. 73, p. 577—623.*

After this experimental determination we tried to get theoretically some further information about the different influences which would determine the effective diameter. The results obtained have also been published in the cited article in the *Ann. der Physik.*



Only an enumeration of the conclusions we thought ourselves justified in making, will be given below.

The piston has a shape as is seen in figure 1; the forces acting on it, may be divided into three groups:

1. the purely hydrostatic forces;
2. forces exerted by the flowing of the liquid which leaks out between axis and mantle;
3. the frictional forces resulting from the descent of the piston.

The forces mentioned under 1 give a result equal to the difference of pressure in the diameters of the lower and the upper part of the piston.

The forces under 2 give as consequence that instead of diameter should be read the arithmetical means between diameter of axis and hole.

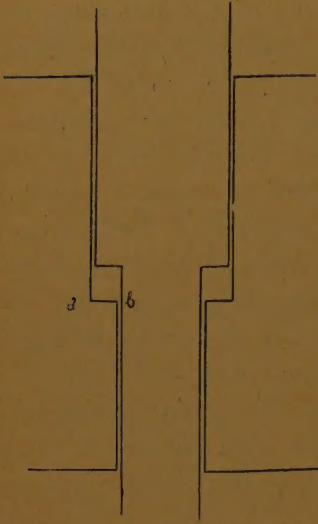


Fig. 1.

The forces under 3 give an apparent increase of diameter which is independent of the pressure, and may be valued in our case at 1/10000 of the original value.

Attention is drawn to the fact that none of the above-mentioned influences appears to be a pressure-function.

Besides, the deformation of piston and hole in consequence of the load is also to be taken into account.

The piston is subject to two variations of form:

1. Transverse contraction of its lower part in consequence of the extension caused by the load.

2. Compression of the two parts of the piston through the pressure. As the pressure in the space between axis and mantle gradually decreases, this compression has not the same value at every height.

The first influence brings about an increase of the effective diameter to an amount of:

$$\frac{3}{2.2 \times 10^7} \times p,$$

the second a diminution of:

$$\frac{7}{2.2 \times 10^7} \times p.$$

The mantle of the hole too extends, the lower hole also undergoing a deformation through the pressure exerted on the plane



$\alpha$ — $b$ . This change of form only gives a modification in consequence of the frictional influence of the oil that leaks away; moreover the compression of the piston contributes to this, which had not yet been taken into account in the calculation of this compression. The two influences can, however, be simply determined together, and then give an increase of the effective diameter to an amount of:

$$\frac{p}{2.5 \times 10^6}$$

All the influences together cause an increase of diameter of:

$$\frac{p}{4.6 \times 10^6}$$

hence a function of the pressure, which for the present still lies quite out of our possibility of observation, even with our maximum load of 250 atm.

With the second pressure balance up to 5000 atm. we had at our disposal, an influence will very certainly demonstrate itself. Before it is possible, however, to take this into account, this apparatus must be studied more thoroughly.

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The first of these is the fact that the  
the second is the fact that the  
the third is the fact that the  
the fourth is the fact that the

All the above are facts which are  
the first of these is the fact that the

the second is the fact that the  
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